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Synthesis and Thermal Behavior of 5-Azido-1,2,4-triazolyl-5-acetic Acid (ATAA)

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Abstract: The title compound, 5-azido-1,2,4-triazolyl-5-acetic acid (ATAA), was synthesized for the first time by Sandmeyer-reaction in a mixed system (including sodium nitrite, sulfuric acid and sodium azide) from 5-amino-1,2,4-triazolyl-5-acetic acid. Its chemical structure was fully characterized via NMR, IR, MS and elemental analyses. Typical TG and DSC curves indicate the thermal behavior of ATAA includes one dehydrating crystal water stage, one melting stage and one obvious melting decomposition stage. The peak temperatures at each stage are 85.6 °C, 168.0 °C and 177.9 °C, respectively. In addition, a novel polynitro-azole energetic compound (5-azido-3-trinitromethyl-1H-1,2,4-triazole) was designed and calculated. The standard enthalpy of formation, the calculated density as well as the detonation velocity are 449.62 kJ · mol⁻¹, 1.91 g · cm⁻³ and 9096 m · s⁻¹, respectively.

Key words: triazole; synthesis; azide; polynitro compound; thermal behavior; 5-azido-1,2,4-triazolyl-5-acetic acid (ATAA)

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1 Introduction

In the field of high energy density materials (HEDMs), the synthesis and development of new energetic materials continue to focus on new heterocycles with high density, high heat of formation, and good oxygen balance (index of the deficiency or excess of oxygen in a compound required to convert all carbon into carbon dioxide, and all hydrogen into water)^[1]. Of particular interest is high-nitrogen structure unit (e.g. triazole) in combination with energetic substituents such as nitro (—NO₂), nitrate (—ONO₂), azido (—N₃) and nitramino (—NHNO₂) functionalities, because these compounds have satisfactory detonation performance^[2-6].

In this article, a novel azido-triazole compound, 5-azido-1,2,4-triazolyl-5-acetic acid (ATAA), was synthesized by Sandmeyer-Reaction from 5-amino-1,2,4-triazolyl-5-acetic acid (**1**) for the first time (Scheme 1). Its structure characterization was performed using infrared (IR), mass spectrum (MS) and elemental analysis as well as multinuclear NMR spectroscopy. The thermal behaviors of ATAA were studied by thermal gravity analysis (TG) and differential scanning calorimetry (DSC). In addition, 5-azido-3-trinitromethyl-1H-1,2,4-triazole (**2**), a novel polynitro-triazole energetic compound derived from ATAA, was designed and calculated. The energetic properties of **2** compared to HMX and its analogue 5-nitro-3-trinitromethyl-1H-1,2,4-triazole (**2i**) of literature [6].

2 Experiment

2.1 Materials and Instrument

All chemical reagents and solvents were obtained from Sigma-Aldrich Inc. or Chengdu Kelong Reagent Company (an-

alytical grade) and used as supplied without further purification. 5-amino-1,2,4-triazolyl-5-acetic acid (**1**) was prepared according to the literature [6] procedure. Infrared spectra were obtained using a Nexus 87 Fourier transform infrared spectroscope (Nicolet USA). Organic elemental composition was analyzed on Vario EL III elemental analyzer (Elementar Germany). Purity analysis with HPLC was carried out on a LC-20A system equipped with a C18 column (250 mm × 4.6 mm, 5 mm, Agela) and a UV detector set at 254 nm (Shimadzu Japan). ¹H NMR (500.13 MHz) and ¹³C NMR (125.76 MHz) spectra were recorded on a V500 spectrometer (Bruker, Germany). Chemical shifts were reported as a δ value in parts per million and tetramethylsilane was used as the internal standard. ¹H NMR and ¹³C NMR spectra were recorded in DMSO-*d*₆.

2.2 Synthesis of ATAA

A solution of sodium nitrite (0.72 g, 10.5 mol, 2.1 equiv) in water (10 mL) was added dropwise to a suspension of **1** (0.71 g, 5 mmol) in 20% sulfuric acid (40 mL) at -10 °C. The mixture was allowed to warm to -5 °C and subsequently a solution of sodium azide (0.5 g, 7.5 mmol, 1.5 equiv) in water (5 mL) was added dropwise for 10 min. Then the suspension was stirred for 2 h at -5 °C. The pink solid was filtered and recrystallized in ethyl acetate. Collection of the colorless precipitate afforded ATAA · H₂O, yielding 0.48 g. The purity was 97.5%. ¹H NMR (DMSO-*d*₆): δ 3.78 (s, 2H), δ 12.39 (s, 1H), 13.81 (s, 1H). ¹³C NMR (DMSO-*d*₆): δ 169.3, 156.2, 151.6, 32.6. IR (KBr, ν/cm⁻¹): 3304 (vs), 2959 (w), 2445 (w), 2148 (vs), 1669 (s), 1550 (m), 1518 (vs), 1442 (m), 1389 (m), 1342 (w), 1263 (w), 1236 (vs), 1138 (w), 1059 (m), 1025 (w), 948 (w), 926 (w), 791 (m), 735 (m), 670 (w), 531 (w), 467 (w), 406 (w). MS (DEI+): *m/z*: 167.0 [C₄H₃N₆O₂]⁻. Elemental analysis (%) calcd for C₄H₄N₆O₂ · H₂O: C 25.81, H 3.25, N 45.15. Found: C 25.84, H 3.24, N 45.13.

2.3 Thermal Decomposition Condition

TGA-DSC was conducted on a TGA/DSC 2 STAR[®] system

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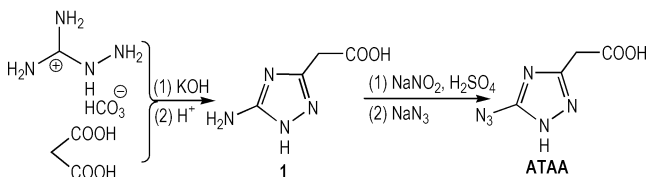
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(Mettler, Switzerland) under an argon atmosphere at a flow rate of $100 \text{ mL} \cdot \text{min}^{-1}$. The sample mass was 0.7 mg and the heating rate was $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The temperature range was from room temperature to $300 \text{ }^\circ\text{C}$.

3 Results and Discussions

3.1 Syntheses

The synthesis starts with commercially available **1**, which was synthesized by intramolecular condensation of malonic acid and aminoguanidine bicarbonate in alkaline medium^[7]. In general the azidation reaction is performed at $0\text{--}5 \text{ }^\circ\text{C}$ ^[8–9]. According to the previously published azidation process, ATAA was synthesized tentatively from **1** through diazotization in sodium nitrite and sulfuric acid at $0 \text{ }^\circ\text{C}$ and subsequent reaction with an excess of sodium azide at $5 \text{ }^\circ\text{C}$. However, a mass of bright red precipitate was generated among the reaction progress. The precipitate was analyzed by thin layer liquid chromatography (TLC), and included three components. These results suggest that the diazonium derived from **1** is unstable and highly reactive at the above temperature range, causing the decrease of reaction selectivity. We infer that decreasing the reaction temperature may have a protective effect on the azidation reaction through reducing side reaction (e. g. azo reaction). Therefore, the diazotization process and the azidation process were controlled at lower temperatures of $-10 \text{ }^\circ\text{C}$ and $-5 \text{ }^\circ\text{C}$. The bright red precipitate was significantly reduced as expected. ATAA was obtained as colorless precipitate, which can be purified by recrystallization in ethyl acetate. The complete synthetic process was shown in Scheme 1.



Scheme 1

3.2 Thermal Behavior of ATAA

As shown in the TGA curve (Fig. 1), it indicates the thermal behavior of ATAA can be divided into one dehydrating crystal water stage and one obvious decomposition stage. The dehydration occurs at $63.9\text{--}109.3 \text{ }^\circ\text{C}$ with a mass loss of about 9.7% , corresponding to the loss of 1 mol water molecule. And this result, which is consistent with that of elemental analysis, has proven further that the exact chemical formula of the title compound is $\text{ATAA} \cdot \text{H}_2\text{O}$. The exothermic decomposition starts at $158.3 \text{ }^\circ\text{C}$ and ends at $201.2 \text{ }^\circ\text{C}$ with a mass loss of about 66.6% . The TGA curve shows almost 80% mass loss.

From Fig. 2, we can see the DSC curve of ATAA is in harmony with the TGA curve, including two endothermic processes and one exothermic process. The first endothermic process is corresponding to the dehydrating crystal water stage, and the dehydration enthalpy (ΔH_e), the extrapolated onset temperature and the peak temperature are $-182.3 \text{ J} \cdot \text{g}^{-1}$, $63.0 \text{ }^\circ\text{C}$ and $85.6 \text{ }^\circ\text{C}$, respectively. The second endothermic

process belongs to the melting stage. The melting enthalpy (ΔH_m), the extrapolated onset temperature and the peak temperature are $-146.4 \text{ J} \cdot \text{g}^{-1}$, $162.1 \text{ }^\circ\text{C}$ and $168.0 \text{ }^\circ\text{C}$. The exothermic process is derived from the decomposition of ATAA, and the decomposition enthalpy (ΔH_d), the extrapolated onset temperature and the peak temperature are $206.4 \text{ J} \cdot \text{g}^{-1}$, $171.2 \text{ }^\circ\text{C}$ and $177.9 \text{ }^\circ\text{C}$. The foregoing data of TGA and DSC shows that the thermal stability of ATAA is excellent among the azido-1,2,4-triazole derivatives^[10–11], which may be due to the strong hydrogen bond system between N—H of triazole and —COOH .

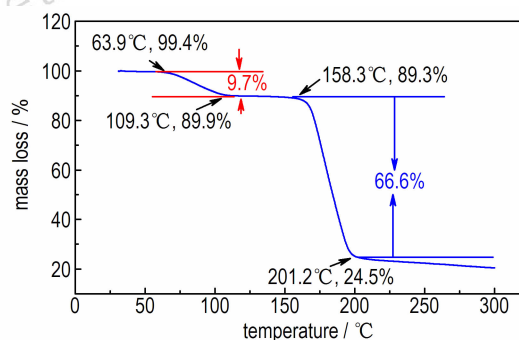


Fig. 1 TGA curves of ATAA at a heating rate of $10.0 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$

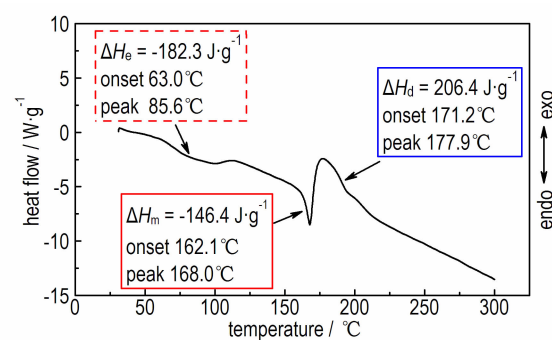
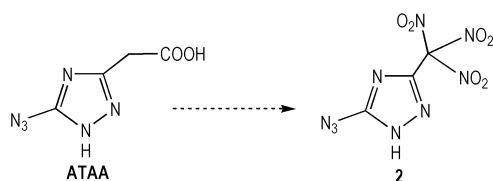


Fig. 2 DSC curve of ATAA at a heating rate of $10.0 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$

3.3 The Detonation Performance

Highly energetic compounds which have polynitro groups are one of the important classes of useful energetic materials^[6, 12]. And azole acetic can be converted into corresponding trinitromethyl azoles by nitration with mixed acids, HNO_3 and H_2SO_4 ^[13]. As such, 5-azido-3-(trinitromethyl)-1*H*-1,2,4-triazole (**2**), the molecule displayed in Scheme 2, is potential via nitration reaction step from ATAA. The detonation performances of **2** were calculated by Monte-Carlo method^[14], Atomization scheme^[15] and Kamlet-Jacobs formula^[16]. These data was listed in the Table 1. The calculated densities, the detonation pressure, as well as the detonation velocity is $1.91 \text{ g} \cdot \text{cm}^{-3}$, 38.67 GPa and $9096 \text{ m} \cdot \text{s}^{-1}$, respectively. These calculated data indicates the detonation performance of **2** is comparable to HMX and its analogues **2i**^[6]. Additionally, **2** has obvious advantage in the stand enthalpies of formation and nitrogen content compare to HMX and **2i**. Our efforts toward the synthesis of the excellent material are currently on going.



Scheme 2

Table 1 Prediction of performance for 2 and 3

com-pound	ρ ¹⁾ /g · cm ⁻³	$\Delta_f H_{(s, M)}^0$ ²⁾ /kJ · mol ⁻¹ /%	N ³⁾ /%	Ω ⁴⁾ /%	D ⁵⁾ /m · s ⁻¹ /GPa	p ⁶⁾ /GPa
2	1.91	449.62	48.65	-3.1	9096	38.67
2i ^[6]	1.92	123.20	37.26	9.12	8983	35.51
HMX ^[17]	1.90	116.00	37.84	-21.61	9221	41.50

Note: 1) density; 2) molar enthalpy of formation; 3) nitrogen content; 4) oxygen balance; 5) detonation velocity; 6) detonation pressure.

4 Conclusions

A novel azido-triazole, ATAA, was synthesized for the first time by Sandmeyer-Reaction from 1. Typical TG and DSC curve indicates the thermal behavior of ATAA includes one dehydrating crystal water stage, one melting stage and one obvious melting decomposition stage. And the peak temperatures at each stage are 85.6 °C, 168.0 °C and 177.9 °C. The detonation performance of 2 derived from ATAA was calculated. The stand enthalpies of formation, the calculated densities as well as the detonation velocity belonging to 2 are 449.62 kJ · mol⁻¹, 1.91 g · cm⁻³ and 9096 m · s⁻¹, respectively.

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5-叠氨基-1,2,4-三唑-5-乙酸(ATAA)的合成及热性能

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摘要: 以 5-氨基-1,2,4-三唑基-5-乙酸(1)为原料,经 Sandmeyer 反应得到一种新型叠氮三唑类化合物 5-叠氨基-1,2,4-三唑-5-乙酸(ATAA)。通过¹H NMR、¹³C NMR、IR 及元素分析等手段对化合物结构进行表征。TG 及 DSC 的研究表明,ATAA 的热行为包括结晶水脱除、熔化及热分解三个过程,每个过程所对应的峰值温度分别为 85.6,168.0 °C 和 177.9 °C。基于 ATAA 设计出一种新型多硝基含能化合物——5-叠氨基-3-硝仿基-1,2,4-三唑(2),并对其爆轰性能进行预估。结果表明其标准生成焓、理论密度及理论爆速分别为 449.62 kJ · mol⁻¹、1.91 g · cm⁻³ 和 9096 m · s⁻¹,整体性能与 HMX 相当。

关键词: 三唑; 合成; 叠氮化合物; 多硝基化合物; 热行为

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