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# Synthesis and Characterization of a Novel Energetic Inner-salt 5,5′-Bis(3-diazo-1,2,4-triazole)

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**Abstract**: A novel energetic inner-salt 5,5′-bis(3-diazo-1,2,4-triazole)(BDTZ) was firstly designed and synthesized via two-step reactions of cyclodehydration and diazotization using oxalic acid and aminoguanidinium bicarbonate as starting materials with a total yield of 53.0%, and its structure was characterized by the means of IR spectrum, NMR and elemental analysis. Based on 3LYP/6-311G+(d,p) level, the estimated density of BDTZ is 1.73 g·cm$^{-3}$, its detonation velocity is 7780 m·s$^{-1}$ and the detonation pressure is 26.72 GPa. The nitrogen content of BDTZ is 74.47%, which contains no toxic heavy metals, showing that BDTZ is a green primary explosive with good detonation performance.

**Key words**: energetic inner-salt; 5,5′-bis(3-diazo-1,2,4-triazole)(BDTZ); synthesis; performance

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## 1 Introduction

Lead azide and lead styphnate are the most commonly used primary explosives today. The long-term use of these compounds has caused considerable lead contamination for environment, which implies that it is necessary to look for greener primary explosives[1]. Nitrogen-rich heterocyclic compounds are new generation primary explosives[2]. Owing to the high positive heats of formation resulting from the large number of N—N and C—N bonds and the high level of environmental compatibility, 1,2,4-triazole energetic compounds have been studied over the last couple of years with growing interest[3-5]. Herein, a novel energetic inner-salt 5,5′-bis(3-diazo-1,2,4-triazole)(BDTZ) was firstly synthesized, and its structure was well characterized by the means of NMR, IR and elemental analysis. Moreover, the performances of BDTZ such as detonation pressure and detonation velocity were calculated by Kamlet-Jacobs formulae[6]. BDTZ, which does not contain toxic heavy metals, exhibits good performances and potentially useful prospect as green primary explosive.

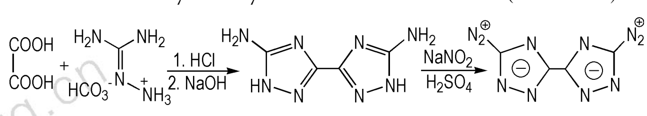
## 2 Experimental

### 2.1 Materials and Instruments

The oxalic acid and aminoguanidinium bicarbonate were of AR grade and purchased from the trade without further purification. $^1$H NMR and $^{13}$C NMR were obtained in DMSO-$d_6$ on a Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000–400 cm$^{-1}$. Elemental analyses (C, H and N) were performed on a VARI-El-3 elementary analysis instrument.

### 2.2 Synthetic Route

Using oxalic acid and aminoguanidinium bicarbonate as starting materials, the title compound BDTZ was firstly synthesized via the reactions of cyclodehydration and diazotization (Scheme 1).




**Scheme 1** The synthetic route of 5,5′-bis(3-diazo-1,2,4-triazole)

### 2.3 Synthesis of 5,5′-Diamino-3,3′-bis-1,2,4-triazole

According to a modified literature procedure[5], hydrochloric acid (25 mL) was added to a stirred mixture of oxalic acid (10.0 g, 79.4 mmol), aminoguanidinium bicarbonate (22.6 g, 166 mmol) and water (25 mL). The reaction mixture was stirred at 70 ℃ for 1 h. After cooling to 40 ℃, the mixture was made alkaline to pH=14 with sodium hydroxide. The reaction mixture was heated at reflux for another 1 h and subsequently acidified with acetic acid to pH=4. The resulting precipitate was collected by filtration, washed with water and dried in vacuum to yield white solid 9.9 g with a yield of 75.1%.

$^1$H NMR(DMSO-$d_6$, 500 MHz): 5.92(s, 4H, $NH_2$), 12.77(s, br, 2H, NH); IR(KBr, $\nu$/cm$^{-1}$): 3407, 3335, 3094, 2862, 2782, 1709, 1663, 1600, 1485, 1457, 1359, 1268, 1105, 1061, 987, 798, 733; Anal. Calcd. for $C_4H_6N_8$(%):

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C 28.92, H 3.64, N 67.44; Found: C 29.16, H 3.70, N 67.14.

### 2.4 Synthesis of 5,5′-Bis(3-diazo-1,2,4-triazole)(BDTZ)

A suspension of 5,5′-diamino-3,3′-bis-1,2,4-triazole (0.50 g, 3.01 mmol) in 20% sulfuric acid (15 mL) was added dropwise to a solution of sodium nitrite (3 equiv., 0.63 g, 9.13 mmol) in water (5 mL) at 0–5 ℃. Then the reaction mixture was stirred at room temperature for 1 h. The resulting white precipitate was filtered, washed with water, and dried in air to yield white solid 0.4 g with a yield of 70.6%.

$^{13}$C NMR (125 MHz, DMSO-$d_6$, $\delta$): 156.411, 136.762; IR(KBr, $\nu$/cm$^{-1}$): 3441, 2277, 2232, 1721, 1402, 1326, 1311, 1275, 1205, 1074, 1016, 970, 706, 655. Anal. Calcd. for $C_4N_{10}$(%): C 25.53, N 74.47; Found: C 25.42, N 73.29.

### 2.5 The Performances of Physico-chymistry and Detonation for BDTZ

The density of BDTZ was computed based on Monte-Caolo method[7-8] using the optimized structure at the B3LYP/6-311G+(d,p) level of theory. The enthalpies of the gas phase species M were computed according to the atomization energy method[9] by using the CBS-4M method. Gas phase enthalpies were transformed to solid state enthalpies by Trouton's rule[10]. Based on the calculated enthalpy of formation and density, the detonation velocity and detonation pressure for BDTZ were calculated by Kamlet-Jacobs formulae[6]. The performances for BDTZ were showed in Table 1.

**Table 1** Comparison of the performances for lead azide and BDTZ

| compound | $\rho$ /g·cm$^{-3}$ | $D_v$ /m·s$^{-1}$ | $D_p$ /GPa | $\Delta_f H_m$ /kJ·mol$^{-1}$ | $Q$ /J·g$^{-1}$ |
|---|---|---|---|---|---|
| BDTZ | 1.73 | 7780 | 26.72 | 1256.7 | 6680.5 |
| $Pb(N_3)_2$[1] | 4.8 | 5920 | 33.8 | 450.1 | 1569 |

Note: $\rho$ is density; $D_v$ is detonation velocity; $D_p$ is detonation pressure; $\Delta_f H_m$ is enthalpy of formation; $Q$ is heat of explosion.

## 3 Conclusions

All tests point to the fact that this material is a suitable and non-toxic replacement for lead azide, with a straightforward synthesis from commonly available chemicals. Above all, a novel energetic inner-salt, 5,5′-bis(3-diazo-1,2,4-triazole) (BDTZ), was designed and synthesized via a two-step reaction process, and its structure was fully characterized for the first time. In addition, some main performances of energetic inner-salt BDTZ were obtained by calculation as follows: Its density is 1.73 g·cm$^{-3}$, detonation velocity is 7780 m·s$^{-1}$ and enthalpy of formation is 1256.7 kJ·mol$^{-1}$.

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# 新型含能内盐5,5′-双(3-重氮基-1,2,4-三唑)合成与表征

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**摘　要：**以草酸与氨基胍碳酸氢盐为原料，经脱水环化、重氮化两步反应首次设计、合成了新型含能内盐5,5′-双(3-叠氮-1,2,4-三唑)(BDTZ)，总收率为53.0%，并采用红外光谱、核磁共振及元素分析对结构进行了表征；基于B3LYP/6-311G+(d,p)水平，预估BDTZ的密度为1.73 g·cm$^{-3}$，爆速为7780 m·s$^{-1}$，爆压为26.72 GPa。BDTZ氮含量为74.47%，不含有毒重金属，表明BDTZ为一种爆轰性能良好的绿色起爆药。

**关键词：**含能内盐；5,5′-双(3-重氮基-1,2,4-三唑)(BDTZ)；合成；性能
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