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Research Article

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Synthesis, morphology and theoretical calculation of *1H*-benzotriazole aceto-hydrazide

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ABSTRACT

1H-benzotriazole aceto-hydrazide(BAH) was synthesized from 1H-Benzotriazole, chloroacetic acid, ethanol and hydrazine using liquid-phase method. The structure of BAH was characterized by FT-IR, ^{1}H NMR. The studies on morphology showed that the most BAH were needle-like, and the average diameter of BAH was 30 μm. Theoretical calculation using Dmol3 indicated the HOMO and LUMO of BAH were -0.179748 eV and -0.098578 eV, respectively. And it was clear that the HOMO of BAH focused on the amide group, However, the LUMO focused on 1H-Benzotriazole. Thermal decomposition of BAH indicated heating rate could affect the decomposition of BAH, the decomposition temperature and mass increased with increasing of heating rate.

Keywords: 1H-benzotriazole, Morphology, Theoretical optimization, Thermal decomposition

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INTRODUCTION

With rapid development of chemical synthesis technology[1-4], many 1H-benzotriazole derivatives with many unique advantages have been synthesized, and these compounds with 1H-Benzotriazole are widely used in more and more important fields such as chemical synthesis [5-7], materials [8-10], water research [11-12], corrosion inhibitors [13-14], etc. For examples, Dharavath Srinivas et al [8] reported that 1H-benzotriazole derivatives with amino, azido, nitro, and nitrogen-rich azole were synthesized to be used in energetic material. And the research results showed that the detonation velocity values calculated for these synthesized compounds ranged from 5.45 to 8.06 kms^{-1}, and the detonation pressure ranged from 12.35 to 28 GPa. Further studies on energetic properties and thermal analyses of some 1H-benzotriazole derivatives revealed a comparable performance to that for TNT and confirmed the potential application of these molecules in the area of energetic materials. Zhang et al [15] synthesized a novel benzotriazole derivative. Benzotriazole derivative displayed anti-proliferative effects on several human tumor cell lines, and the results suggest that benzotriazole derivative could inhibit BEL-7402 cell proliferation, and the cell death could occur through the modulation of mitochondrial functions regulated by reactive oxygen species. Li et al [16] reported three *S*-(1H-benzotriazole-1-yl) methyl *N*, *N*-dialkyldithiocarbamates were synthesized and evaluated their tribological behaviors as additives in rapeseed oil by using a four-ball tester. The results indicated that the additives possessed excellent load-carrying abilities and high thermal stabilities, but did not have antiwar and friction-reducing properties.

Thus, with development of studies on 1H-Benzotriazole and its derivatives, more and more 1H-benzotriazole derivatives will be synthesized, and their application field also will be widened. However, researchers need investigate more information including structure, morphology, thermal stability of 1H-Benzotriazole derivatives to further wide their application field, and make 1H-Benzotriazole derivatives play a more important role in wider fields. In this paper, we synthesized 1H-benzotriazole aceto-hydrazide(BAH), the theoretical calculation of BAH

was carried out by Dmol3, and the HOMO and LUMO levels of BAH were deduced. And the morphology and thermal stability of BAH were investigated.

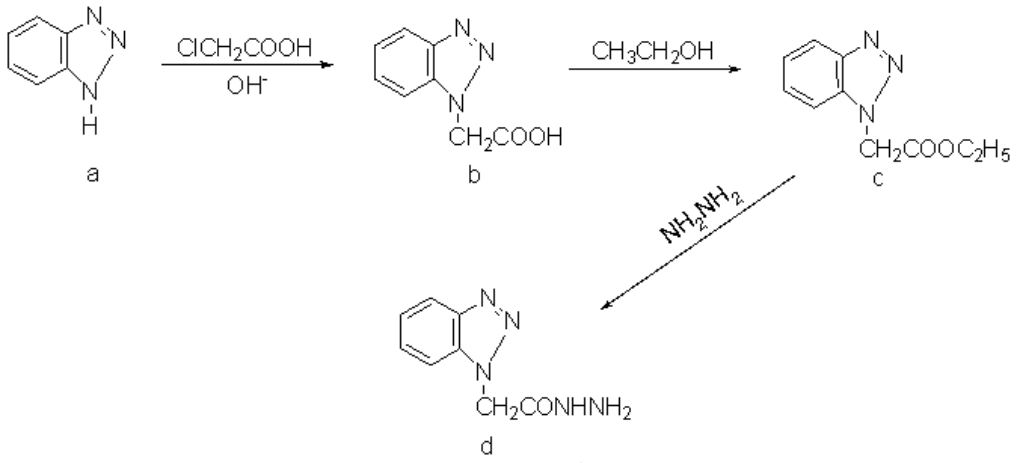
EXPERIMENTAL SECTION

The materials including 1H-Benzotriazole, chloroacetic acid, sodium hydroxide, ethanol, hydrazine were of analytical grade. And hydrochloric acid was of chemical grade.

Fourier transform infrared spectra(FT-IR) was recorded on a Bio-Rad FTS135 spectrophotometer from 4000 to 400 cm^{-1}. The BAH sample was mixed with KBr powders and pressed into a disk suitable for IR measurement. The ^1H nuclear magnetic resonance(^1H NMR) was recorded on Brucker AVANCE 300 spectrometers. The solvent was dimethyl sulphoxide (DMSO).The morphologies of the fracture surfaces of samples were examined by XL-30 ESEM FEG, Philips, in 15-20 kV accelerating voltage (Tungsten filament). The samples were fractured and covered by gold vapors.

Synthesis procedure of BAH

BAH was prepared as shown in Scheme-1. 1H-Benzotriazole, chloroacetic acid, sodium hydroxide, water of 100ml were mixed, and the mixture was heated up to reflux, and held for 3h. White deposition(b) was obtained by acidizing via hydrochloric acid after cooling to room temperature. Then, product b, ethanol and a little sulfuric acid were mixed, and the mixture was heated up to reflux for 4h, the reaction mixture was poured onto ice water, and put in the refrigerator overnight, obtained product b. Finally, product c, hydrazine and ethanol were mixed to heat up to reflux for 3h, the BAH was obtained after cooling to room temperature.



Scheme-1 Synthesis of BAH

RESULTS AND DISCUSSION

Structures of BAH

The FT-IR spectra of BAH is shown in Fig.1. In the spectra, the peaks at 3331.8 cm^{-1} and 3063.8 cm^{-1} contributes to the absorption of N-H stretching vibration, and the absorption peak at 2935.8 cm^{-1} belongs to O-H stretching vibration, the absorption peak at 1658.1 cm^{-1} contributes to C=O stretching vibration. Then the absorption peaks at 1607.1 cm^{-1}, 1496.6 cm^{-1} and 1457.3 cm^{-1} prove the existence of benzene. The peak at 1546.2 cm^{-1} and 1228.1 cm^{-1} are C-N-H bending vibration absorption and C-N stretching vibration respectively, and the absorption at 1416 cm^{-1} contributes to N=N bending vibration. The absorption peak at 1316.6 cm^{-1} is mixed peak including C-N stretching vibration and N-H bending vibration absorption, and 774.9 cm^{-1} and 752.3 cm^{-1} contribute to C-H rocking vibration and bending vibration respectively. FT-IR spectrum analysis showed that the infrared spectrum dates of BAH was consist with the structure of BAH.

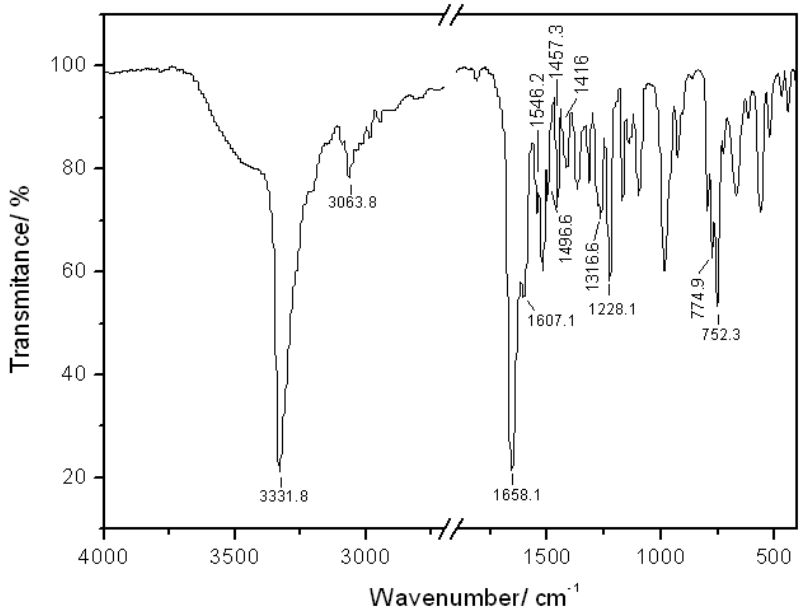


Figure 1 IR spectra of BAH

In order to further confirm the structure of BAH, ^{1}H NMR was used to investigate the structure of BAH. The ^{1}H NMR patterns of BAH is depicted in Fig.2. The single peak at δ_H=9.64 is proton resonance peak of N-H, the multiple peaks at δ_H=7.38-8.06 are proton resonance peaks of benzene, the peak at δ_H=5.40 is proton resonance peak of CH_2, the peak at δ_H=4.40 is NH_2 proton resonance peak. NMR analysis further confirms the structure of BAH.

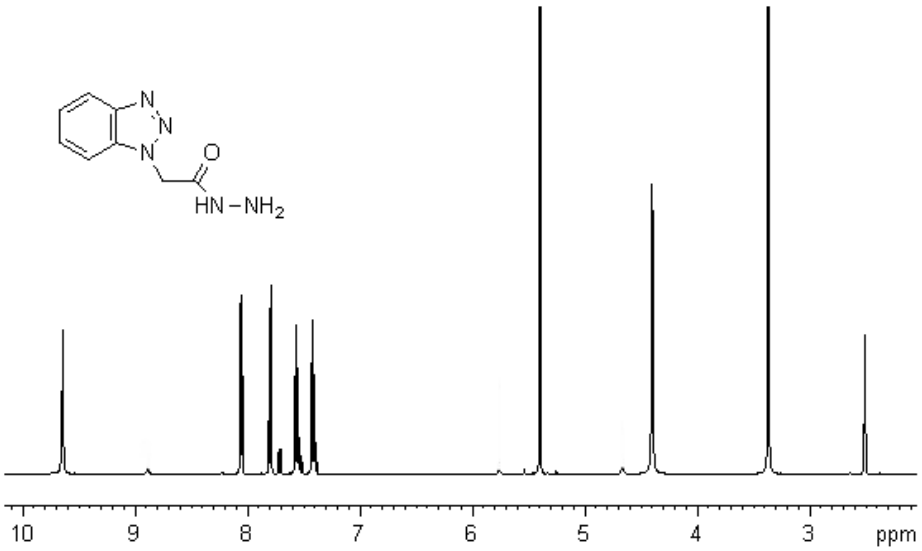


Figure 2 ^{1}H NMR of BAH

Morphology and theoretical structure of BAH

Fig.3 is SEM images of BAH (B is the partly amplificatory images of A respectively). The SEM images show that the most BAH are needle-like, and the ratio of length and diameter is very large. In addition, as shown in Figure.3B, the average diameter of BAH is 30 μm, and the surface of BAH is very smooth, which indicated that the crystal growth of BAH synthesized by liquid phase reaction method is very prefect.

At same time, theoretical calculation is very useful method to investigate the structure of compounds [17]. Thus, the theoretical calculation was carried out by using Dmol3. Fig.4 shows that the optimized geometry structure, HOMO and LUMO of BAH, the theoretical calculation indicates the HOMO and LUMO of BAH are -0.179748 eV and -0.098578 eV, respectively. And it is clear that the HOMO of BAH focus on the amide group, However, the LUMO focus on the 1H-Benzotriazole. In addition, the electron density and potentials of BAH also were calculated, and the result was listed in Fig.5. Fig.5 shows that the electron density of BAH is very homogeneous in geometry structure.

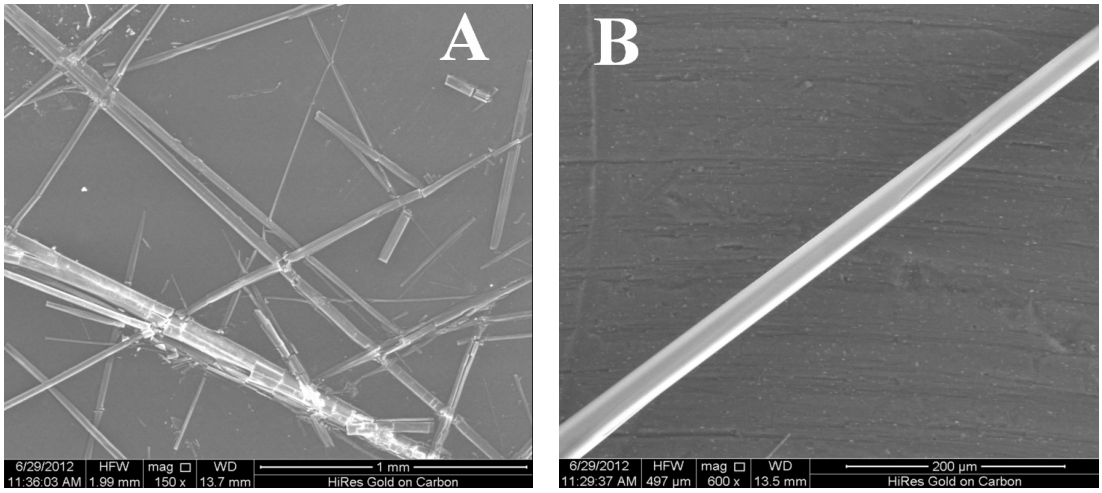


Figure 3 SEM of BAH

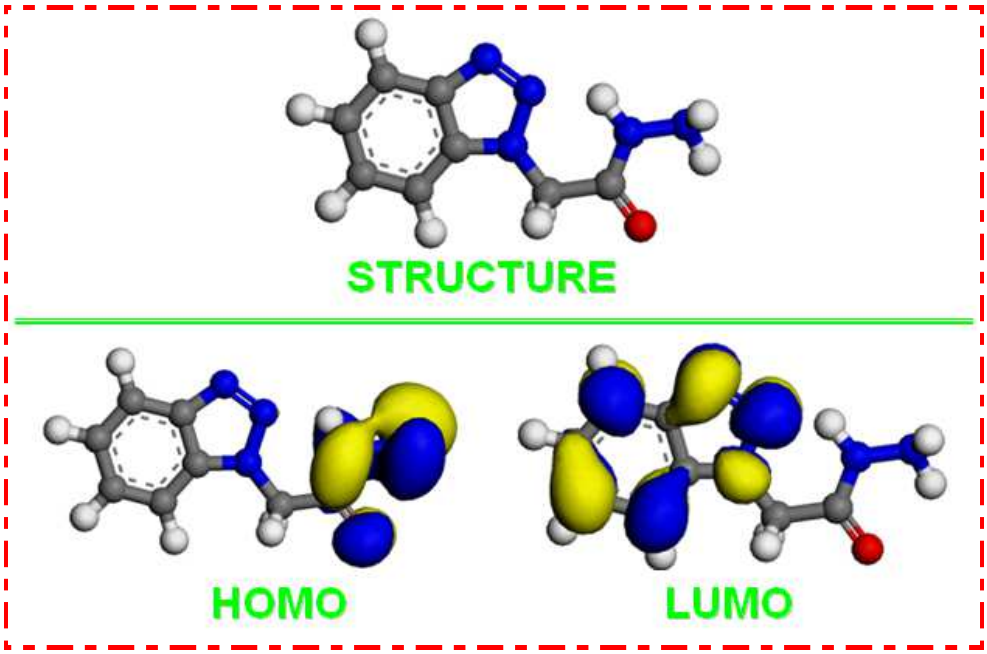


Figure 4 Optimized structure of BAH

Thermal decomposition of BAH

Studies on the thermal decomposition of materials is very important research field[18-20], because the thermal properties can significantly affect the application of materials. Thus, the thermal decomposition of BAH also is investigated. Fig.6 shows the TGA curves of BAH with a heating ramp of 5, 10, 15℃/min under nitrogen flow from 100 to 600℃. As seen in Fig.6, there exist two platform on TGA curves at heating rate of 5℃/min. However, there exists only one platform at heating rate of 10, 15℃/min, this result indicates that heating rate can affect the decomposition of BAH, and the lower heating rate makes the decomposition of BAH become more clear. At same time, it is clear that decomposition temperature significantly increased with increasing of heating rate, the reason is that rapid heating rate makes decomposition of BAH not achieve at set temperature, at the same time, the temperature has get into the following set temperature, resulting in decomposition achieving at higher temperature. The decomposition temperature of BAH at heating rate of 5, 10, 15℃/min are 245.1, 165.7 and 288.3℃ respectively, which show good thermal stability of BAH. In addition, different heating rate also can result in different decomposition mass, similarly the decomposition mass increase with increasing of heating rate.

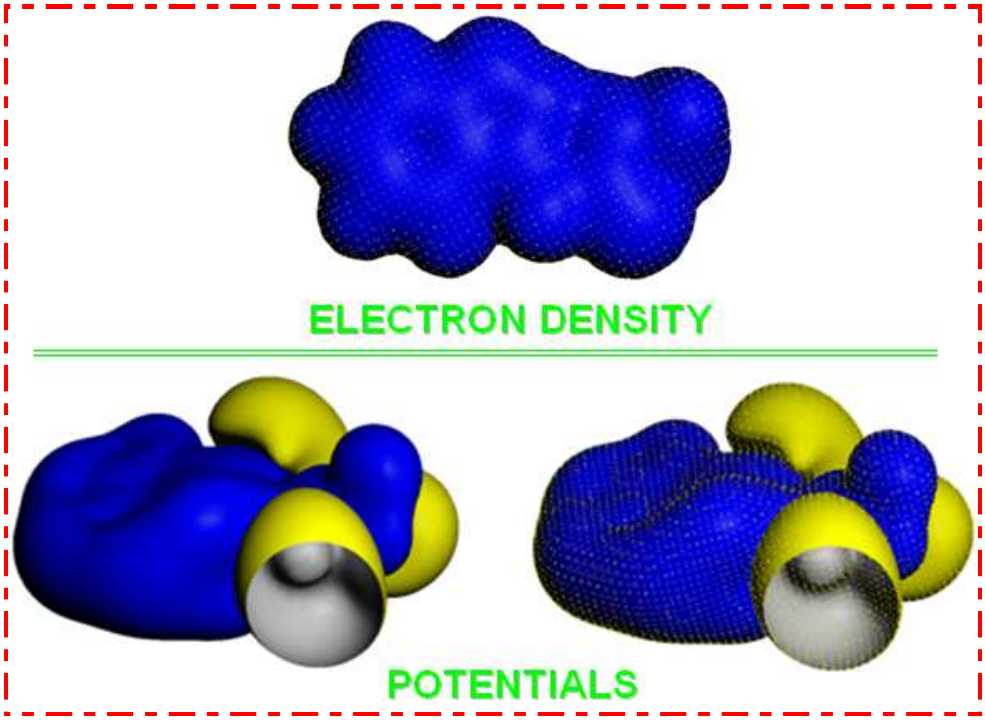


Figure 5 Electron density and potentials of BAH

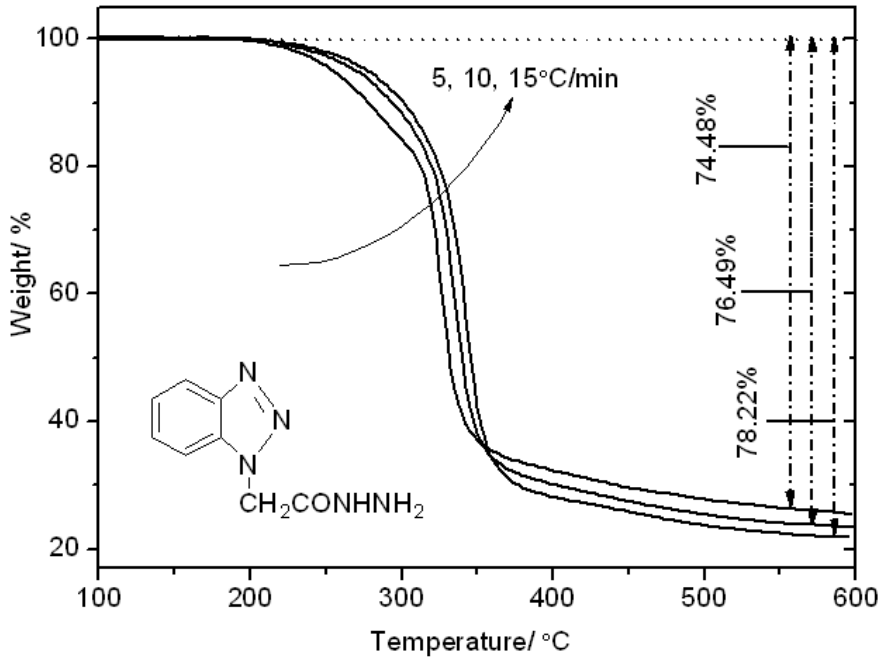


Figure 6 Thermal decomposition of BAH

CONCLUSION

BAH was synthesized by three step reaction, and the morphology, thermal stability and theoretical calculation were investigated. The most BAH were needle-like. Theoretical calculation indicated the HOMO of BAH focused on the amide group, however, the LUMO focused on the 1H-Benzotriazole. Thermal decomposition of BAH indicated heating rate can affect the decomposition of BAH.

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