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Article

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# Exothermic or Endothermic Decomposition of Disubstituted Tetrazoles was Tuned by Substitution Fashion and Substituents

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**Abstract:** Nitrogen-rich compounds such as tetrazoles are widely used as candidates in gas generating agents. However, the detailed study on the differentiation of the two isomers of disubstituted tetrazoles are rarely studied, which is very important information for design advanced materials based on tetrazoles. In this article, pairs of 2,5- and 1,5-disubstituted tetrazoles were carefully designed and prepared for the study on their thermal decomposition behavior. And the substitution fashion of 2,5- and 1,5- and the substituents at C-5 position were found to affect the endothermic or exothermic properties. This is for the first time to the best of our knowledge that the thermal decomposition properties of different tetrazoles could be tuned by substitution ways and substitute groups, which could be used as a useful platform to design advanced materials for temperature-dependant rockets. And the Aza-Claisen rearrangement was proposed to understand the endothermic decomposition behavior.

# 1. Introduction

Energy release under control is the central task in the area of energetic materials[1-9]. Nitrogen-rich materials are widely used in the field of rockets, missiles, artillery, and gas generating agents, which require the materials to have low sensitivity and produce hot gases and glowing particles in a short time. Tetrazoles are a family of nitrogen-rich heterocycles and have attracted considerable attention in many areas including pharmaceuticals[10], energetic materials[11], [12], porous materials[13], fuel cells[14] and so on. Particularly, tetrazole moiety has become a strategic group in the applications such as gas generating agents[7], [15], [16], propellants and so forth, since tetrazoles generate two molecules of nitrogen per ring upon decomposition and have high thermal stability and non-explosive character. Take 5-amino-1H-tetrazole as an example, it is studied as a burn rate modifier, fire suppressor and an environmental friendly gas generating agent. However, there're very few examples of tetrazoles developed for gas generating agent besides 5-amino-1H-tetrazole and G15B (Figure **1a**).

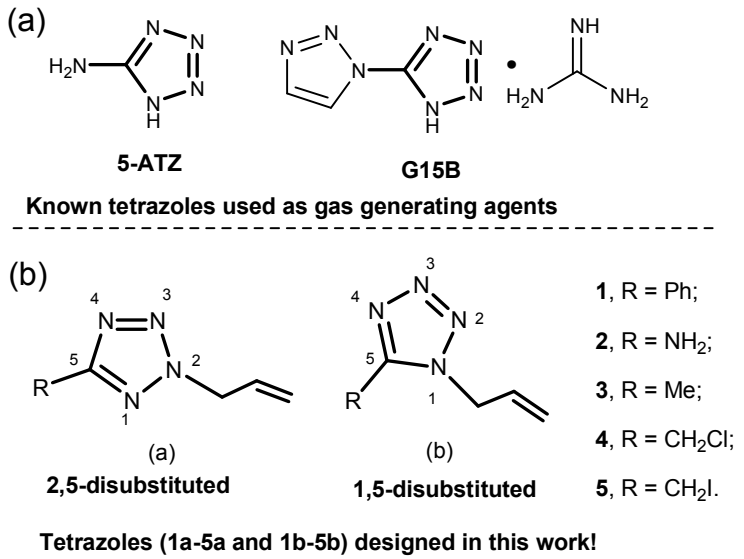



Figure**1** Known tetrazoles used as gas generating agents (a); and New tetrazoles designed in this work for the energy release control (b).

Considering the gas generator system requires control of temperature and pressure in different applications, we wonder if we can make the tetrazole derivatives to realize the control. Actually, the tautomerisation between 1H- and 2H- tetrazole was well documented[17], and two isomers of 2,5- and 1,5-disubstituted tetrazoles exist for the disubstituted tetrazoles. The thermal decomposition studies on tetrazole materials indicated that N-alkyl tetrazole had better thermal stability than the original tetrazole[18]. Moreover, it is reported that 2-alkyl tetrazole was less thermostable than its isomeric 1-alkyl tetrazole[19], which is attributed by the different decomposition pathway. However, the further differences between the two isomers of disubstituted tetrazoles were rarely studied.

In this article, we report the design, syntheses, fully characterization and thermal decomposition properties of 5 pairs of disubstituted tetrazoles (Figure **2b**) with *N*-allyl group, which can be readily introduced and converted to many functional group based on the derivatization of C=C double bond.

## 2. Experimental Section

Causions: Tetrazoles and their derivatives are potential explosives, which may be sensitive to environmental stimuli such as impact, friction heat and electrostatic discharge. While we encountered no problems in handling of these materials, appropriate precausions and proper protective measures (safety glasses, face shields leather coats, Kevlar gloves and ear protectors) should be taken when preparing and manipulating these materials.

All reagents were used as received from commercial sources without further purification or prepared as described in the literature. 5-phenyl-1H-tetrazole, 5-amino-1H-tetrazole and 5-methyl-1H-tetrazole are supplied by Zhongshenghuateng Co. Ltd in Beijing, China. 5-chloromethyl-1H-tetrazole is prepared by following a known procedure. Reactions were stirred using Teflon-coated

magnetic stir bars. Analytical TLC was performed with 0.20 mm silica gel 60F plates. Chromatographic purification of products was carried out by flash chromatography on silica gel (230-400 mesh). NMR spectra were measured in $CDCl_3$ (with TMS as internal standard) or DMSO-d6 on a Bruker AV400 or Varian INOVA-400M ($^1H$ at 400 MHz, $^{13}C$ at 100 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hz. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution EI mass spectra (HR-EI-MS) were recorded on an GCT CA127 Micronass UK mass spectrometer, and High-resolution ESI mass spectra (HR-ESI-MS) on Thermo Q exactive mass spectrometer. Thermo-gravimetric-analysis-Mass spectrometry (TGA-MS) was measured by NETZSCH STA449C / MS403C.

**2.1 The synthesis of 2-allyl-5-phenyltetrazole (1a) and 1-allyl-5-phenyltetrazole (1b):** 5-phenyl-tetrazole (2 mmol, 292 mg) in acetone (10 ml) was added anhydrous sodium carbonate (2.4 mmol, 255 mg) , the resulting mixture was stirred at room temperature for 30 min, and then treated with allyl bromide (4.0 mmol, 484 mg) in acetone (10 ml). The reaction mixture was heated to reflux at 60 $^oC$ for 2 h, and then acetone was removed by vacuum, the residue was solved in water and extracted by ethyl acetate, the combined organic layer was dried with anhydrous sodium sulfate and concentrated to give oily residue, which purified through column chromatography to afford 2-allyl-5-phenyl-tetrazole (**1a**, yield 79%) and 1-allyl-5-phenyl-tetrazole (**1b**, yield 17%).

*2-allyl-5-phenyl-tetrazole*(**1a**)*:* Rf = 0.69 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3037 (w), 3034 (w), 2984 (w), 1645 (w), 1529 (m), 1465 (s), 1450 (s), 1380 (w), 1336 (s), 1279 (s), 1200 (m), 1177 (w), 1136 (w), 1073 (m), 1044 (m), 1027 (m), 989 (m), 983 (m), 789 (s), 733 (s), 694 (s), 590 (w); $^1H$ NMR (400 MHz，$CDCl_3$) δ (ppm): 8.112 (d, 2H, *J* = 6.0 Hz), 7.409 (q, 3H, *J* = 7.4 Hz), 6.004~6.102 (m, 1H), 5.332 (d, 1H, *J* = 1.2 Hz), 5.299 (d, 1H, *J* = 5.2 Hz), 5.177 (d, 2H, *J* = 6.0 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ (ppm): 165.09, 130.17, 129.85, 128.75, 127.30, 126.70, 120.57, 55.22; HRMS (EI): *m/z* 186.0909 $[M]^+$ ($C_{10}H_{10}N_4$, required 186.0905).

*1-allyl-5-phenyl-tetrazole* (**1b**)*:* Rf = 0.39 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3083 (w), 3059 (w), 3034 (w), 1645 (w), 1067 (w), 1576 (w), 1539 (m), 1462 (s), 1426 (w)1407 (m), 1288 (m), 1252 (m), 1141 (m), 1109 (m), 1074 (w), 993 (s), 934 (s), 780 (s), 762 (s), 696 (s), 591 (m); $^1H$ NMR (400 MHz, $CDCl_3$) δ (ppm): 7.670 (d, 2H, *J* = 6.0 Hz), 7.520 (q, 3H, *J* = 7.52

Hz), 5.976~6.071 (m, 1H), 5.332 (d, 1H, *J* = 10.4 Hz), 5.081 (d, 1H, *J* = 17.2 Hz), 5.029 (d, 2H, *J* = 5.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 154.51, 131.41, 130.63, 129.27, 128.73, 123.70, 119.71, 50.07; HRMS (EI): m/z 186.0908 $[M]^+$ ($C_{10}H_{10}N_4$, required 186.0905).

**2.2 The synthesis of 2-allyl-5-aminotetrazole (2a) and 1-allyl-5-aminotetrazole (2b)：** Achieved by a similar procedure to 1a and 1b, but using 5-amino-1H-tetrazole (3.0 mmol, 309 mg) as starting material.

*2-allyl-5-amino-tetrazole*(**2a**) (117 mg, yield 31%) *:* Rf = 0.54 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/1]; IR (KBr, $cm^{-1}$)：3331 (s), 3150 (s), 3034 (w), 2979 (w), 1680 (s), 1661 (s), 1606 (s), 1593 (vs), 1474 (m), 1432 (m), 1332 (m), 1281 (w), 1211 (w), 1134 (m), 1087 (w), 987 (m), 792 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.987~6.067 (m, 1H), 5.364(d, *J* = 10.4 Hz, 1H), 5.344 (d, *J* = 4.8 Hz, 1H), 5.011 (d, J = 4.8 Hz, 2H), 4.397 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 166.44, 130.10, 120.76, 55.29; HRMS (ESI): m/z 126.07739 $[M+H]^+$ ($C_4H_8N_5$, required 126.07797).

*1-allyl-5-amino-tetrazole*(**2b**) (204 mg, yield 54%)*:* Rf = 0.13 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/1]; IR (KBr, $cm^{-1}$)：3090 (w), 2940 (m), 2861 (m), 2274 (vs), 1686 (vs), 1648 (m), 1529 (s), 1468 (vs), 1424 (s), 1338 (m), 1252 (m), 1121 (w), 1085 (w), 990 (s), 938 (m),782(m); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.881 ~ 6.006 (m, 1H), 5.416 (d, *J* = 10.0 Hz, 1H), 5.172 (d, *J* = 17.2 Hz, 1H), 4.978 (d, *J* = 3.2 Hz, 2H), 4.813 (s, 2H); HRMS (ESI): m/z 126.08509 $[M+H]^+$ ($C_4H_8N_5$, required 126.07797).

**2.3 The synthesis of 2-allyl-5-methyltetrazole (3a) and 1-allyl-5-methyltetrazole (3b):** achieved by a similar procedure to 1a and 1b, but using 5-methyl-1H-tetrazole (168 mg, 2 mmol) as starting material.

*2-allyl-5-methyl-tetrazole* (**3a**) (127.5 mg, yield 37%)*:* Rf = 0.62 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3090 (w), 2989 (w), 2942 (w), 2860 (w), 1648 (w), 1506 (s), 1424 (m), 1394 (m), 1371 (w), 1335 (w), 1198 (m), 1174 (m), 1077 (m), 1033 (s), 991 (s), 939 (s), 800 (s), 716 (w), 671 (w), 576 (w); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.980~6.079 (m, 1H), 5.363 (d, 1H, *J* = 4.0 Hz), 5.330 (d, 1H, *J* = 13.2 Hz), 5.133 (d, 2H, *J* = 6.0 Hz), 2.507 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.19, 129.98, 120.86, 55.20, 10.94; HRMS (ESI): *m/z* 125.0822 $[M+H]^+$ ($C_5H_8N_4$, required 125.0827).

*1-allyl-5-methyl-tetrazole* (**3b**) (92.5 mg, yield 51%)*:* Rf = 0.10 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3088 (w), 3034 (m), 2986 (m), 1647 (w), 1521 (m), 1461 (s), 1424 (s), 1339 (w), 1243 (w), 1216 (m), 1110 (m), 990 (s), 941 (s), 786 (s),740 (w), 714 (w), 654 (w), 603 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.864~5.946 (m, 1H), 5.321 (d, 1H, *J* = 10.4 Hz), 5.107 (d, 1H, *J* = 17.2 Hz), 4.906 (d, 2H, *J* = 5.6 Hz), 2.498 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.77, 129.85, 119.90, 49.44, 8.91; HRMS (ESI): *m/z* 125.0822 $[M+H]^+$ ($[C_5H_8N_4$, required 125.0827).

**2.4 The synthesis of 2-allyl-5-chloromethyltetrazole (4a) and 1-allyl-5-chloromethyltetrazole (4b):** achieved by a similar procedure to 1a and 1b, but using 5-chloromethyl-1H-tetrazole (337 mg, 2 mmol) as starting material.

*2-allyl-5-chloromethyl-tetrazole* (**4a**) (197 mg, yield 62%)*:* Rf = 0.61 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3089 (w), 3030 (w), 2986 (w), 1647 (m), 1499 (s), 1430 (s), 1398 (w), 1338 (m), 1269 (s), 1207 (m), 1172 (w), 1080 (w), 1031 (s), 990 (s), 942 (s), 804 (vs), 742 (m), 664 (m), 608 (w), 579 (w); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.981~6.081 (m, 1H), 5.372 (d, 1H, *J* = 6.0 Hz), 5.338 (d, 1H, *J* = 12.8 Hz), 5.183 (d, 2H, *J* = 6.4 Hz), 4.743 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.24, 129.43, 121.46, 55.68, 34.20; HRMS (ESI): m/z 159.0430 $[M+H]^+$ ($CH_4N_5$, required 159.0438).

*1-allyl-5-chloromethyl-tetrazole* (**4b**) (83 mg, yield 26%)*:* Rf = 0.20[*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3088 (w), 3034 (m), 2986 (m), 1647 (w), 1521 (m), 1461 (s), 1424 (s), 1339 (w), 1243 (w), 1216 (m), 1110 (m), 990 (s), 941 (s), 786 (s), 740 (w), 714 (w), 654 (w), 603 (m); $^1$H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.911 ~ 6.065 (m, 1H), 5.377 (d, 1H, *J* = 10.0 Hz), 5.284 (d, 1H, *J* = 17.2 Hz), 5.066 (d, 2H, *J* = 6.0 Hz), 4.789 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.52, 129.27, 121.11, 50.42, 31.32; HRMS (ESI): m/z 159.0433 $[M+H]^+$ ($CH_4N_5$, required 159.0438).

**2.5 The synthesis of 2-allyl-5-iodomethyltetrazole (5a) and 1-allyl-5-iodomethyltetrazole (5b)**: A solution of 1-allyl-5-chloromethyl-tetrazole (2 mmol, 317 mg) in acetone (10 ml) and water (10 ml) was added potassium iodide (4 mmol, 664 mg), the resulting mixture was heated at 60 $^o$C for 8 h. Then the solvent was removed by vacuum, the residue was solved in water and extracted by ethyl acetate, the combined organics were dried with anhydrous sodium sulfate, concentrated, the residue was purified through column chromatography to give 1-allyl-5-iodomethyl-tetrazole (366.5 mg,

yield 73%). By a similar procedure, 2-allyl-5-iodomethyltetrazole was synthesized from 2-allyl-5-chlroromethyltetrazole (2 mmol, 317 mg).

*2-allyl-5-iodomethyl-tetrazole* (**5a**)*:* Rf = 0.64 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3087 (w), 3039 (m), 2985 (m), 1646 (m), 1492 (s), 1424(s), 1390 (m), 1337 (m), 1291 (w), 1206 (m), 1172 (s), 1099 (m), 1078 (m), 1027 (m), 989 (s), 940 (s), 797 (s), 717 (m), 679 (w), 555 (m);$^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.009~6.108(m, 1H), 5.409(d, 1H, *J* = 10.4 Hz), 5.375(d, 1H, *J* = 16.8 Hz), 5.185(d, 2H, *J* = 4.8 Hz), 4.511(s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.60, 129.55, 121.40, 55.67, -13.18; HRMS (ESI): m/z 250.9775 $[M+H]^+$ ($CH_4N_5$, required 250.9794).

*1-allyl-5-iodomethyl-tetrazole* (**5b**) (406.6 mg, yield 81%)*:*: Rf = 0.28 [*V* (EtOAc)/*V* (Petroleum Ether) = 1/2]; IR (KBr，$cm^{-1}$): 3087 (w), 3035 (m), 2982 (m), 1646 (m), 1516 (s), 1458 (s), 1420 (s), 1338 (w), 1306 (w), 1244 (m), 1166 (s), 1091 (s), 989 (s), 940 (s), 780 (m), 746 (w), 710 (m), 689 (w), 553 (m); $^{1}$H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.009~6.108(m, 1H), 5.409(d, 1H, *J* = 10.4 Hz), 5.375(d, 1H, *J* = 16.8 Hz), 5.185(d, 2H, *J* = 4.8 Hz), 4.511(s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ (ppm): 164.60, 129.55, 121.40, 55.67, -13.18; HRMS (ESI): m/z 250.9775 $[M+H]^+$ ($CH_4N_5$, required 250.9794).

## 3. Results and Discussions

### 3.1 The synthesis of disubstituted tetrazoles

A few synthetic strategieswere developed towards tetrazoles, including tetrazole itself, mono-substituted tetrazole, disubstituted tetrazoles[20-25], ionic tetrazoles[26-28] and tetrazole-based complex[29-32]. Among them, the Click strategy is the most important way[23], [25], [33], which required the starting materials with cyano (or isocyanate) and azido group. In addition, new chemistry based on C-H and C-C cleavage have been reported[24], as well as copper catalyzed N-arylation[22](see Table S5). Recently, some green chemistry has been developed towards the preparation of tetrazoles[34-39]. As for as synthesis of disubstituted tetrazoles is concerned, 1,5-disubstituted tetrazoles[23-25], [33], [40] and 2,5-disubstituted tetrazoles[22], [34], [41] are synthesized

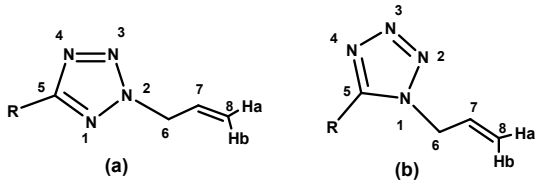
efficiently respectively. We chose the *N*-allylation reactions[20], [21], [41] on 5-substituted tetrazoles, in order to get both 1-allyl-5-substituted tetrazole and 2-allyl-5-substituted tetrazole from one reaction without using noble metal and in low cost. Firstly, we investigated on the reaction conditions based on *N*-allylation of 5-phenyltetrazole (see Table S1 in supporting information), and we found heating was necessary for high conversion of starting materials, as well as at least 2 equivalents of allyl bromide. By doing the reaction in acetone, the 2-allyl-5-phenyltetrazole and 1-allyl-5-phenyltetrazole were obtained in good overall yield up to 99% yield, with 2,5-disubstituted tetrazole as major product (Table S2 in SI). In order to see if possible to vary the ratio of two isomers, we also studied the solvent effects on the outcome of the ratio of **1a** to **1b** (see table S2 in SI). Among the solvents screened, toluene and 1,2-dichloroethane gave no products owing to poor solubility of 5-phenyltetrazole in them, other solvents such as DMF, THF and acetonitrile gave similar results as acetone, ethanol gave the ratio of 3.7 to 1 based on the crude $^{1}$H-NMR spectra (Figure S1-S4). Considering the ease of the reaction, we chose the condition of $Na_2CO_3$/Acetone/60 $^{o}$C, and the *N*-allylations were achieved on 5-phenyltetrazole, 5-methyltetrazole and 5-chlorotetrazole (Table 1). Under the reaction conditions, although 5-phenyltetrazole gave **1a** and **1b** in a ratio of 79:17, 5-methyltetrazole gave **2a** and **2b** in an isolated yield of 37% and 51%, 5-chloromethyltetrazole gave **3a** and **3b** in an isolated yield of 62% and 26%. The total yield was 96%, 88% and 88% respectively for tetrazoles **1**, **2** and **3**. Afterwards, chloro in compounds **3a** and **3b** was substituted by iodide to give the corresponding iodide **5a** and **5b**.

## 3.2 The structure characterization of disubstituted tetrazoles

All the new tetrazoles were fully characterized by TLC, FT-IR, $^{1}$H-NMR, $^{13}$C-NMR and HR-MS. During the reactions, we found the two isomers could be separated easily, since they have

big polarity differences in TLC[21] (Table S3 in SI). 2,5-disubstituted tetrazole **a** had higher Rf value [Rf > 0.6, 33% EtOAc in PE) than its corresponding 1,5-disubstituted tetrazole **b** (Rf<0.39, see Table S3). By looking at the $^{1}$H-NMR and $^{13}$C-NMR spectra of all the disubstituted tetrazoles carefully, we are delighted to find some obvious differences between two isomers (Table **2**). In the $^{1}$H-NMR spectra, the chemical shifts differences between H-8a and H-8b were 0.03 ppm for the 2,5-disubstituted tetrazoles (0.04 ppm for iodide **5a**). The corresponding differences were 0.08 to 0.25 ppm for 1,5-disubstituted tetrazoles. In the $^{13}$C-NMR spectra, the chemical shifts of C-5 in 2,5-disubstituted tetrazoles were higher than 162 ppm, while less than 155 ppm for 1,5-disubstituted tetrazoles. It is characteristic 10 ppm higher for 2,5-disubstituted tetrazole than its corresponding 1,5-disubstituted tetrazole.

**Table 1** The differences of NMR spectra between isomers of disubstituted tetrazoles




| Compound | | 2-Allyl-5-substituted tetrazole (**a**, ppm) | | | | | | 1-Allyl-5-substituted tetrazole (**b**, ppm) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **R=** | **δH6** | **δH8a** | **δH8b** | **Δδ** | **δC5** | | **δH6** | **δH8a** | **δH8b** | **Δδ** | **δC5** |
| **1** | **-Ph** | 5.18 | 5.33 | 5.30 | 0.03 | 165.1 | | 5.03 | 5.33 | 5.08 | 0.25 | 154.5 |
| **2** | **-$NH_2$** | 5.01 | 5.36 | 5.34 | 0.02 | 166.4 | | 4.98 | 5.42 | 5.30 | 0.12 | NA |
| **3** | **-$CH_3$** | 5.13 | 5.36 | 5.33 | 0.03 | 163.2 | | 4.91 | 5.32 | 5.11 | 0.21 | 151.8 |
| **4** | **-$CH_2Cl$** | 5.18 | 5.37 | 5.34 | 0.03 | 163.3 | | 5.07 | 5.38 | 5.28 | 0.10 | 151.5 |
| **5** | **-$CH_2I$** | 5.18 | 5.40 | 5.36 | 0.04 | 164.6 | | 5.01 | 5.42 | 5.34 | 0.08 | 152.7 |
| | **Δδ =δH8a−δH8b** | | | | | | | | | | | |

Through the above differences, the differentiation of 1,5- and 2,5-disubstituted tetrazole could be realized easily based on $^{13}$C-NMR Spectra. To further confirm the substitution fashion, the C-H HMBC experiments of **1a** and **1b** were performed. There's no cross peak seen between C-5 and H6 for 2,5-disubstituted fashion (Figure **2a**), while obvious cross peak between C-5 and H6 was seen in the 1,5-disubstituted fashion (Figure **2b**).

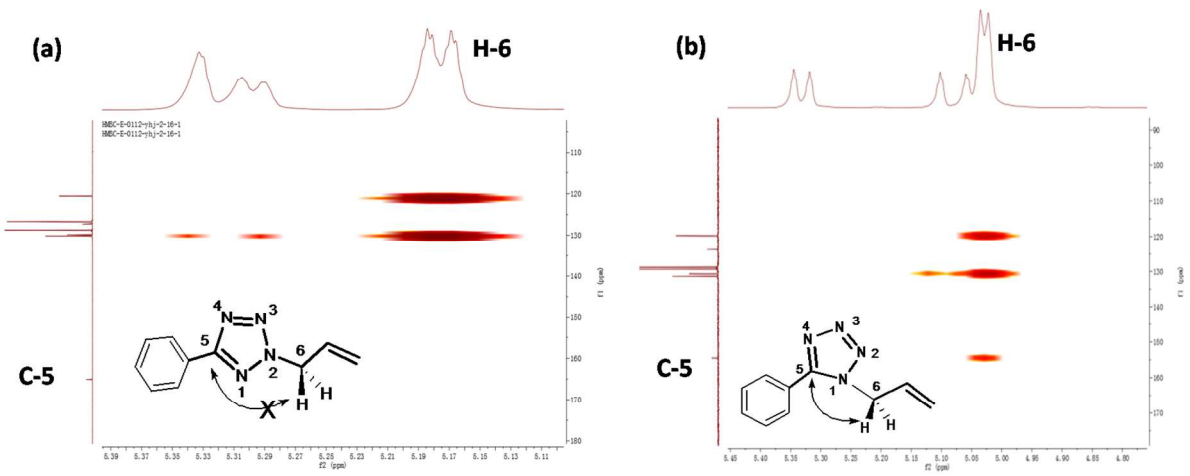



Figure **2** C-H HMBC of 2-allyl-5-phenyltetrazole **1a** and 1-allyl-5-phenyltetrazole **1b** recorded in $CDCl_3$

Similarly, the C-H HMBC experiments on **4a** and **4b** confirmed the correct structure (See Figure S37 and S38 in ESI). In order to further confirm the structure of the disubstituted tetrazoles, we

tried growing single crystals of this class of compounds. Fortunately, the single crystal of 5-amino-2-allyltetrazole (**2a**) was obtained by slow evaporation of solvents, and the X-Ray diffraction was performed, and its structure was shown as Fig 3.

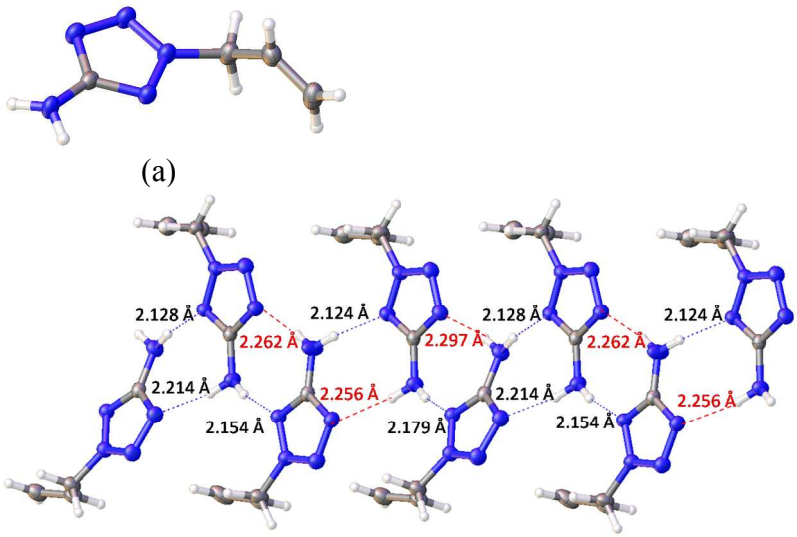



Figure **3** The X-Ray determined molecule structure of 5-amino-2-allyltetrazole (**2a**) and molecular packing through intermolecular H-bond between $NH_2$ and $N^1$, $N^4$ of tetrazole.

Compound 2a crystallizes in an orthorhombic P c a $2_1$ space group , the parameters were shown in Table S4 in SI. Its crystal structure determination revealed clearly that the tetrazole ring was in a 2,5-substitution fashion (see Figure **3a**). Interestingly, each two molecules of tetrazoles were packed in a head-to-tail fashion though H-bond between $NH_2$, $N^1$ of a second tetrazole ring and $N^4$ of the third tetrazole ring (see Figure **3b**). The distance between the proton and nitrogen is in the range of 2.1-2.3 Å. This kind of intermolecular H-bond may contribute to the crystallization and packing in the crystalline.

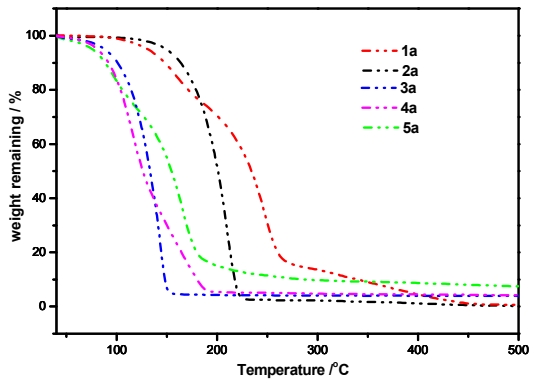
The result of two products 1,5- and 2,5-disubstituted tetrazoles could be explained by the isomerization of 1-NH and 2-NH form of 5-substiuted tetrazole[17]. Especially in the presence of base, the NH of 5-substituted tetrazole was deprotonated to give 1-$N^-$ and 2-$N^-$ of 5-substituted

tetrazole. When they reacted with electrophile, both 1,5- and 2,5-disubstituted tetrazoles were obtained.

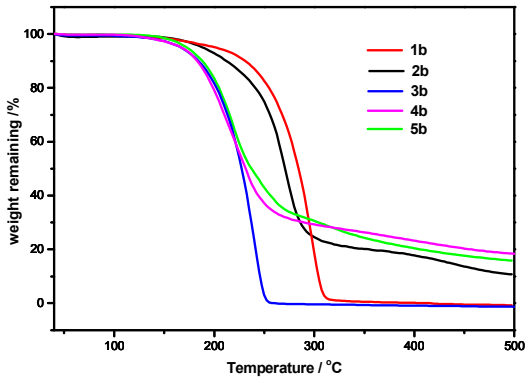
With the confirmation of the above compounds' chemical structure, we moved to the investigation of their thermal decomposition properties.

### 3.3 The thermal decomposition properties of disubstituted tetrazoles

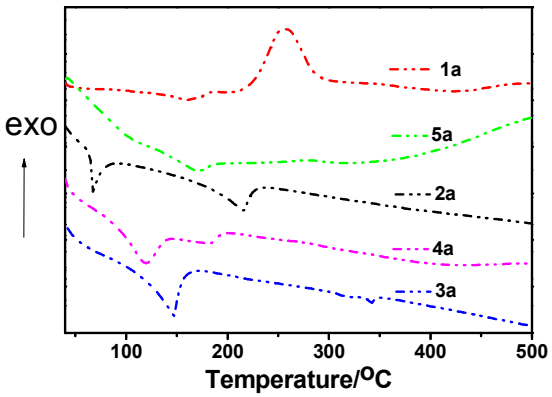
The thermal decomposition was carried out using TGA under nitrogen purge and with a heating rate of 10 $^{o}$C/min. As shown in Figure 4, the 5-phenyltetrazole had $T_{5\%}$ of 217 $^{o}$C, 1-allyl-5-phenyltetrazole (**1b**) has $T_{5\%}$ of 202 $^{o}$C, while 2-allyl-5-phenyltetrazole (**1a**) has much lower $T_{5\%}$ of 147 $^{o}$C. As far as the $T_{max}$ is concerned, 5-phenyltetrazole gave $T_{max}$ of 327 $^{o}$C, 1-allyl-5-phenyltetrazole (**1b**) has $T_{max}$ of 297 $^{o}$C, while 2-allyl-5-phenyltetrazole (**1a**) has much lower $T_{max}$ of 250 $^{o}$C (Figure S39). It is noteworthy that "heat shielding effect"[19] of alkyl group was introduced to explain why the *N*-alkyl tetrazoles had better thermal stability than their original tetrazoles. *However, it is not the case here: 1,5-disubstituted tetrazole was similar or less thermal stable than its original 5-substituted tetrazole, while 2,5-disubstituted tetrazole was obviously less thermal stable.*



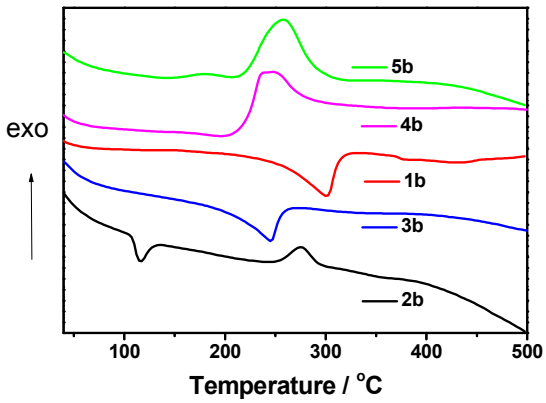

(a) TGA of 1a-5a




(b) TGA of 1b-5b




(c) DSC of 1a-5a




(d) DSC of 1b-5b

Figure **4** TGA of 1a-5a (a), TGA of 1b-5b (b), DSC of 1a-5a and DSC of 1b-5b.

**2a** and **2b** have melting point of 67.4 °C and 117.4 °C respectively (Figure S40), and **2a** and **2b** started to decompose at 150 °C and 187 °C respectively, decomposed at 210 °C and 272 °C maximally. Interestingly, **2a** absorbed heat of 170.8 J/g during decomposition, while **2b** released heat of 246.7 J/g during decomposition.

**3a** and **3b** started to decompose at 87 °C and 167 °C respectively (Figure S41). **3a** and **3b** Decomposed at 145 °C and 245 °C maximally. Interestingly, both **3a** and **3b** released heat during decomposition, the value is 217 and 308 J/g respectively.

**4a** and **4b** started to decompose at 80 °C and 167 °C respectively (Figure S42). **4a** and **4b** decomposed at 115 °C and 215 °C maximally. **4a** absorbed heat of 128.4 J/g during decomposition at 200-300 °C, while **4b** released heat of 697.0 J/g during decomposition at 100-250 °C. It is obvious that the heat change observed from DSC was delayed compared with TGA, owing to the heat transport.

**5a** and **5b** started to decompose at 75 °C and 172 °C respectively (Figure S43). **5a** and **5b** decomposed at 165 °C and 220 °C maximally. **5a** released heat of 527.6.4 J/g during decomposition at 150-320 °C, while **5b** absorbed heat during decomposition at 100-400 °C.

Furthermore, the decomposition of 5-phenyltetrazole was accompanied by two stages, whereas 1-allyl-5-phenyltetrazole (**1b**)only showed one stage of decomposition, while 2-allyl-5-phenyltetrazole (**1a**) three stages. The above observation was summarized in Table **2**.

Table **2** Thermal decomposition properties of disubstituted tetrazoles

| Compound | R | $T_{5\%}$/℃ | | $T_{max}$/℃ | | Energy change [c] (J/g) | |
|---|---|---|---|---|---|---|---|
| | | **a**[a] | **b**[b] | **a** | **b** | **a** | **b** |
| **1** | -Ph | 130 | 202 | 247 | 297 | +260.1 | -205.7 |
| **2** | $-NH_2$ | 150 | 187 | 210 | 272 | -246.7 | -170.8 |
| **3** | $-CH_3$ | 87 | 167 | 145 | 245 | -217.3 | -308.1 |
| **4** | $-CH_2Cl$ | 80 | 167 | 115 | 215 | -128.4 | +697 |
| **5** | $-CH_2I$ | 75 | 172 | 165 | 220 | <0 [d] | +527.6 |

a, 2,5-disubstituted tetrazole; b, 1,5-disubstituted tetrazole; c, "-" represents absorb energy during decomposition, "+" represents release energy during decomposition; d, the peak is too broad to get the accurate energy value.

It can be seen from Table **2** that the *2,5-disubstituted tetrazoles decomposed at lower temperature than their corresponding 1,5-disubstituted isomers for each pair*. E.g., **1a** has $T_{5\%}$ of 130 $^{o}$C, which is 72 $^{o}$C lower than **1b**, **1a** has $T_{5\%}$ of 247 $^{o}$C, which is 50 $^{o}$C lower than **1b**. Similarly, the $T_{5\%}$ difference of 37 $^{o}$C, 80 $^{o}$C, 87 $^{o}$C and 97 $^{o}$C was observed for the two isomers of 2-5, respectively. The difference of 50 $^{o}$C, 62 $^{o}$C, 100 $^{o}$C, 100 $^{o}$C and 55 $^{o}$C for the $T_{max}$ of two isomers of 1-5, respectively. As far as the influence of substituent at C-5 of tetrazole on the thermal stability is concerned, amino and phenyl group gave the highest thermal stability among the disubstituted tetazoles investigated, methyl, chloromethyl and iodomethyl group gave lower stability. Take the $T_{5\%}$ of 2,5-disubstituted tetrazoles as example, 5-amino and 5-phenyl tetrazoles have $T_{5\%}$ of 150 and 130 $^{o}$C, while 5-methyl and 5-chloromethyl and 5-iodomethyl tetrazoles have $T_{5\%}$ of 87, 80 and 75 $^{o}$C. For the $T_{5\%}$ of 1,5-disubstituted tetrazoles, 5-amino and 5-phenyl tetrazoles have $T_{5\%}$ of 187 and 202 $^{o}$C, while 5-methyl and 5-

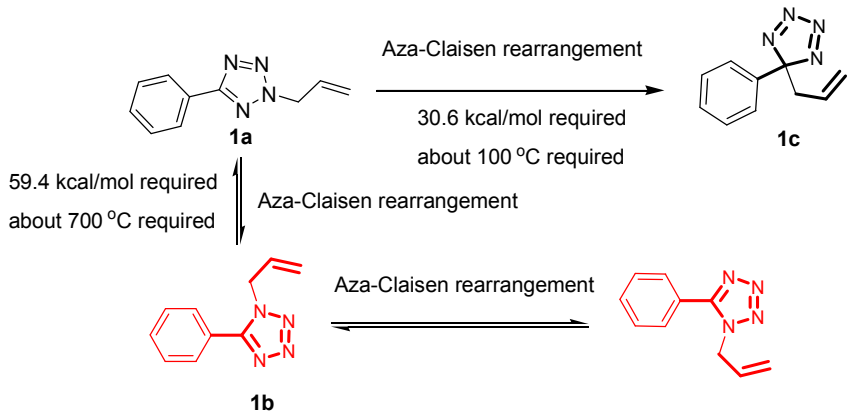
chloromethyl and 5-iodomethyl tetrazoles have $T_{5\%}$ of 167, 167 and 172 $^{o}$C. Similarly, for the $T_{max}$ of 2,5-disubstituted tetrazoles, 5-amino and 5-phenyl tetrazoles have $T_{max}$ of 210 and 247 $^{o}$C, while 5-methyl and 5-chloromethyl and 5-iodomethyl tetrazoles have $T_{max}$ of 145, 115 and 165 $^{o}$C, for the $T_{max}$ of 1,5-disubstituted tetrazoles, 5-amino and 5-phenyl tetrazoles have $T_{max}$ of 272 and 297 $^{o}$C, while 5-methyl and 5-chloromethyl and 5-iodomethyl tetrazoles have $T_{max}$ of 245, 215 and 220 $^{o}$C. The high thermal stability of 5-amino tetrazoles **2a** and **2b**, must be the result of the intermolecular hydrogen bonding between protons of amino group and nitrogen in tetrazole rings, as shown by **2a**'s crystal structure (Figure **3**). The similar higher thermal stability of **1a** and **1b** was contributed by the phenyl ring.

The substitution effect at C-5 of disubstituted tetrazole on the exo- or endo-thermic property is very obvious. When amino group and methyl group were suited at C-5, both 2,5- and 1,5-disubstituted tetrazoles absorbed heat during decomposition. While when phenyl or chloromethyl group were situated at C-5, the two isomers of 2,5-disubstituted tetrazole and 1,5-disubstituted tetrazole performs completely different, one absorbed heat and the other released heat.

In addition, the tetrazoles were found stable when it was exposed to UV light (254 nm) in the air for 30 mins by TLC analysis. These observations will be very useful to design the tetrazole materials for energetic applications, such as gas generators, where temperature was required to adjust. For example, in the cases required exothermic process, 2,5-disubstituted tetrazole **1a** could be used. In the cases of endothermic process, 1,5-disubstituted tetrazole **1b** could be chosen, or 5-amino-tetrazole **2a** and **2b** are good candidates.

## 3.4 The understanding of thermal decomposition properties of disubstituted tetrazoles

For the pair of disubstituted tetrazoles, why they have different decomposition behavior during decomposition? It must be related to its bond-cleavage pathway during decomposition. In order to get some insight on understanding the possible mechanism, **1a** and **1b** were subjected to TG-MS measurement (see Figure S44 and S45 in SI). It showed that both **1a** and **1b** gave off nitrogen gas (molecular weight of 28) and phenyl (molecular weight of 77). In addition, very similar decomposition products were seen from TG-MS spectra. Considering the cleavage of chemical bonds usually gave off heat, the endothermic decomposition must be related to other process. And the aza-Claisen rearrangement is considered for both isomers of tetrazoles to give **1c** (Scheme 1) before decomposition, and the aza-Claisen rearrangement was endothermic reaction. And this process made the whole decomposition endothermic. The Gaussian calculation showed 30.6 kcal/mol for transformation from **1a** into **1c** (see Figure S46 in SI), which is possible to occur at 100 °C.




Scheme 1 The possible aza-Claisen rearrangement occurred at high temperature

## 4. Conclusions

In summary, the preparation of both isomers of disubstituted tetrazoles, precise structure characterization, as well as study on the thermal decomposition behavior were achieved. Based

on the Rf value differences and chemical shifts of C-5 of tetrazoles, it is easy to tell the difference between the pair of isomer. The thermal decomposition behavior of disubstituted tetrazoles was dramatically influenced by different substituent group at C-5 of disubstituted tetrazoles. In addition, when the substituent group is defined at C-5 position, the variation between 2,5- and 1,5-substitution fashion could be used to tune the energy release process. This observation was reported for the first time to the best of our knowledge, and will open a way to design gas generating agents in the future. The aza-Claisen rearrangement was proposed to help the endothermic decomposition process. The further study on the understanding the mechanism and application of these tetrazoles are being carried out in our lab, the relevant results will be reported in due course.

**Supporting Information**. Additional FT-IR, $^{1}$H-NMR, $^{13}$C-NMR, HR-MS, TGA, DSC, TG-MS and Tables for Rf values. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest should be addressed.

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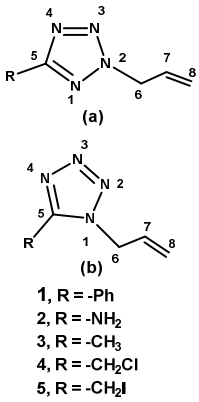
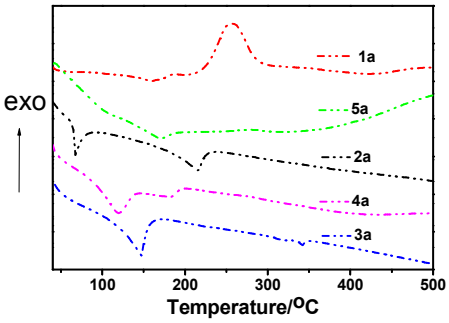
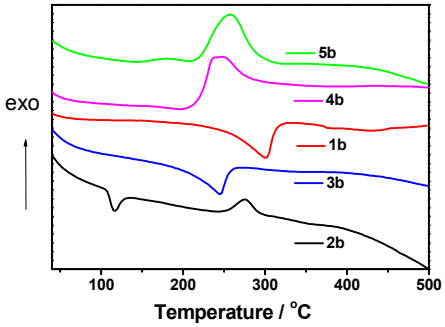
# Table of Contents Graphic

Five pairs of 2,5- and 1,5-disubstituted tetrazoles were carefully designed and prepared for the study on their thermal decomposition behavior. And the substitution fashion of 2,5- and 1,5- and the substituents at C-5 position were found to affect the endothermic or exothermic properties. This could be used as a useful platform to design advanced materials such as temperature-dependant rockets.




DSC of 1a-5a




DSC of 1b-5b