

## Influence of Substituent on Thermal Decomposition of 1H-1,2,4-Triazole

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**Abstract.** The thermal decomposition of 1H-1,2,4-triazole (1Htri) and its derivatives with different substituents were studied by sealed-cell differential scanning calorimetry (SC-DSC). Molecular orbital calculations (MO) were used to clarify thermal and chemical properties. The thermal decomposition temperature ( $T_{DSC}$ ) increased as (1Htri-NO<sub>2</sub>) < (1Htri-NH<sub>2</sub>) < (1Htri-CH<sub>3</sub>) < (1Htri-COOH) < (1Htri). The activation energy ( $\Delta E_a$ ) was determined using the Kissinger and Ozawa approaches. The  $\Delta E_a$  increased as (-NO<sub>2</sub>) < (-NH<sub>2</sub>) < (-CH<sub>3</sub>) < (-COOH) and corresponded with the order of the  $T_{DSC}$ . The MO indicated that the 1Htri-NH<sub>2</sub> and 1Htri-CH<sub>3</sub> decompose at N1-N2 and C3-N4, while 1Htri-COOH and 1Htri-NO<sub>2</sub> decompose at C5-N1 and C3-N4.

**Keywords:** substituent, 1H-1,2,4-triazole, thermal decomposition temperature

### 1. Introduction

An azole is a class of five-membered nitrogen and carbon heterocyclic ring compounds. Its application in gaseous form is expected to increase as it generates minimal toxic substances and has a low environmental impact.

Since more than 50 wt% of triazole consists of nitrogen and a large amount of nitrogen gas is generated during its decomposition, this compound could be used as a gas generating agent by coordination with an appropriate substituent or metal [1–4]. However, the effect of the substituent on the characteristic energy generation has not yet been clarified. If these effects were understood, it would be possible to expand and control the application of these energy-providing materials.

The effect of nitrobenzene substituents has been reported on in terms of the relationship between the thermal decomposition temperature ( $T_{DSC}$ ) and substituent constant [5]. The  $T_{DSC}$  is higher for electron-withdrawing substituents such as (-NO<sub>2</sub>), (-COOH) and (-Cl) and lower for electron-donating substituents such as (-NH<sub>2</sub>), (-OH), (-OCH<sub>3</sub>) and (-CH<sub>3</sub>) as p-substituted nitrobenzene. In this study, the influence of the (-NO<sub>2</sub>), (-COOH), (-CH<sub>3</sub>) and (-NH<sub>2</sub>) substituents on the thermal decomposition of 1H-1,2,4-triazole was determined. The molecular structures of 1Htri and its derivatives are shown in Fig. 1.

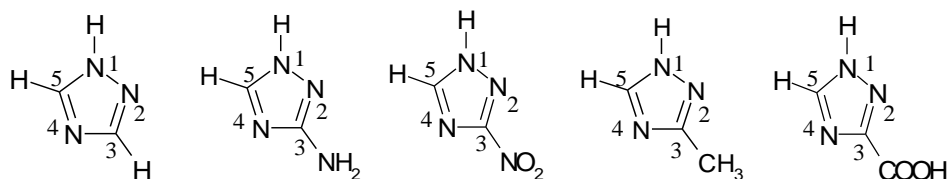


Fig. 1: Molecular structures of 1Htri and its derivatives.

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The  $T_{DSC}$  of 1Htri, 3-amino-1,2,4-triazole (1Htri-NH<sub>2</sub>) and 3-nitro-1,2,4-triazole (1Htri-NO<sub>2</sub>), 3-methyl-1H-1,2,4-triazole (1Htri-CH<sub>3</sub>) and 3-carboxylic acid-1,2,4-triazole(1Htri-COOH) was determined by SC-DSC. To obtain an improved understanding of the thermal behaviour of 1Htri and its coordination with the substituent, molecular orbital calculations (MO) were used to clarify compounds' thermal and chemical properties.

## 2. Experimental

### 2.1. Materials

1Htri, 1Htri-NH<sub>2</sub> and 1Htri-NO<sub>2</sub> (all 98.0%, Tokyo Chemical Industry ), 1Htri-CH<sub>3</sub> (95%, Wako Pure Chemical Industries) and 1Htri-COOH (Wako Pure Chemical Industries) were used in the test work.

### 2.2. Thermal Analysis

To investigate the thermal decomposition, SC-DSC (6220 SII nanotechnology) was carried out in a stainless steel cell at a heating rate of 10 K min<sup>-1</sup> from 30 to 500 °C under a steady state flow of air using a 1.0 mg sample.

### 2.3. Molecular Orbital Calculations

To obtain an understanding of the thermal and chemical properties of 1Htri when coordinated with a substituent, MO were conducted using the Spartan'08 and Gaussian'09 programs. Geometric optimization of the structures and vibration analyses were achieved using unrestricted B3LYP/6-31+G\* density functional theory (DFT). The influence of substituent on (1) electrostatic charge, Mulliken charge and natural charge, (2) dipole moment and (3) bond distance were determined.

## 3. Results and Discussion

### 3.1. Thermal Decomposition

The SC-DSC results are summarized in Table 1. The  $T_{DSC}$  of 1Htri, (1Htri-NH<sub>2</sub>), (1Htri-NO<sub>2</sub>), (1Htri-CH<sub>3</sub>) and (1Htri-COOH) was 348, 296, 279, 310 and 342 °C, respectively. The  $T_{DSC}$  of the substituted 1Htri increased as (1Htri-NO<sub>2</sub>) < (1Htri-NH<sub>2</sub>) < (1Htri-CH<sub>3</sub>) < (1Htri-COOH) < (1Htri). The influence of substituent on thermal decomposition increased as (-COOH) < (-CH<sub>3</sub>) < (-NH<sub>2</sub>) < (-NO<sub>2</sub>).

### 3.2. Activation Energy from SC-DSC

The activation energy ( $\Delta E_a$ ) was determined using the Kissinger [6] and Ozawa [7] approaches with formulae given in (1) and (2), respectively.  $\beta$  is the heating rate [K min<sup>-1</sup>],  $T_p$  is the exothermic peak temperature [K] and R is the gas constant [J K<sup>-1</sup> mol<sup>-1</sup>]. The results are shown in Table 2. The values calculated by the Kissinger method are similar to those obtained using the Ozawa method. The  $\Delta E_a$  decreases with substitution of the 1Htri with (-NH<sub>2</sub>), (-NO<sub>2</sub>), (-CH<sub>3</sub>) and (-COOH). The  $\Delta E_a$  and  $T_{DSC}$  show good agreement (see Fig. 2).

Table 1: Summary of SC-DSC results.

Sample	Step	Thermal effect	Temperature range [°C]	$T_{DSC}$ [°C]	$T_p$ [°C]
1Htri	1	endothermic	120-143	348	370
	2	exothermic	324-422		
1Htri-NH <sub>2</sub>	1	endothermic	154-176	296	323
	2	exothermic	291-393		
1Htri-NO <sub>2</sub>	1	endothermic	218-234	279	360
	2	exothermic	234-388		
1Htri-CH <sub>3</sub>	1	endothermic	44-83	310	356
	2	exothermic	300-461		
1Htri-COOH	1	endothermic	141-174	342	387
	2	exothermic	337-489		

Table 2:  $\Delta E_a$  obtained by Kissinger and Ozawa approaches.

		$\Delta E_a$ [kJ/mol]
1Htri	Kissinger	276
	Ozawa	272
1Htri-NH <sub>2</sub>	Kissinger	126
	Ozawa	136
1Htri-NO <sub>2</sub>	Kissinger	126
	Ozawa	129
1Htri-CH <sub>3</sub>	Kissinger	134
	Ozawa	137
1Htri-COOH	Kissinger	161
	Ozawa	164

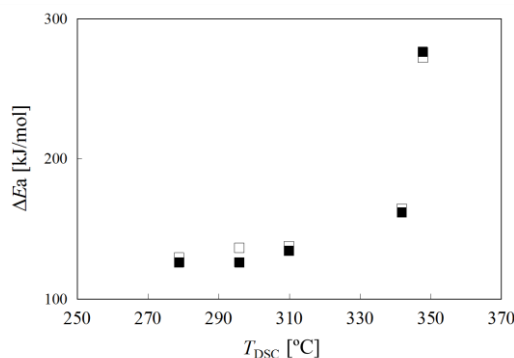


Fig. 2: Relationship between  $\Delta E_a$  and  $T_{DSC}$ . ■Kissinger, □Ozawa

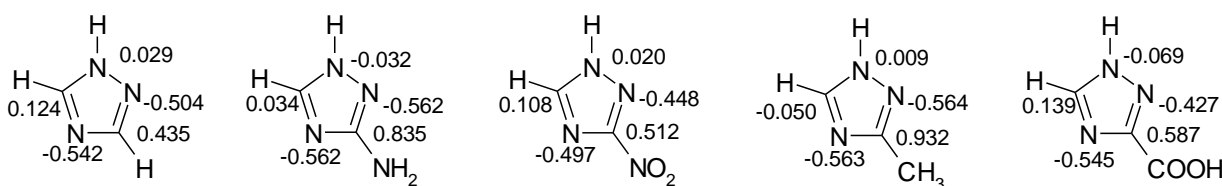


Fig. 3: Electrostatic charge at carbon and nitrogen of 1Htri with each substituent.

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{RA}{\Delta E_a}\right) - \frac{\Delta E_a}{R} \frac{1}{T_p} \quad (1)$$

$$\log \beta = \log \frac{A\Delta E_a}{RF(\alpha)} - 2.315 - 0.4567 \frac{\Delta E_a}{RT_p} \quad (2)$$

### 3.3. Molecular Orbital Calculations

The thermal and chemical properties of 1Htri and its derivatives were studied using MO. We simulated the influence of substituent on (1) electrostatic charge, Mulliken charge and natural charge [8], (2) dipole moment and (3) bond distance.

(1) electrostatic charge, Mulliken charge and natural charge

The influence of the substituent at C3 of 1Htri with regards to electrostatic charge is shown in Fig. 3. The electrostatic charge of 1Htri at N2 and N4 shows a large negative charge relative to the other atoms in 1Htri. The charges of 1Htri at N2 and N4 are (−0.504) and (−0.542), respectively. The 1Htri shows preferable coordination at N2 and N4 with cationic molecules [9]. The N2 and N4 became more negatively charged with (−NH<sub>2</sub>) and (−CH<sub>3</sub>) substituents. The negative values at the N2 and N4 of the 1Htri-NH<sub>2</sub> were (−0.562) and (−0.562), respectively. For 1Htri-CH<sub>3</sub>, the N2 and N4 values were (−0.564) and (−0.563), respectively.

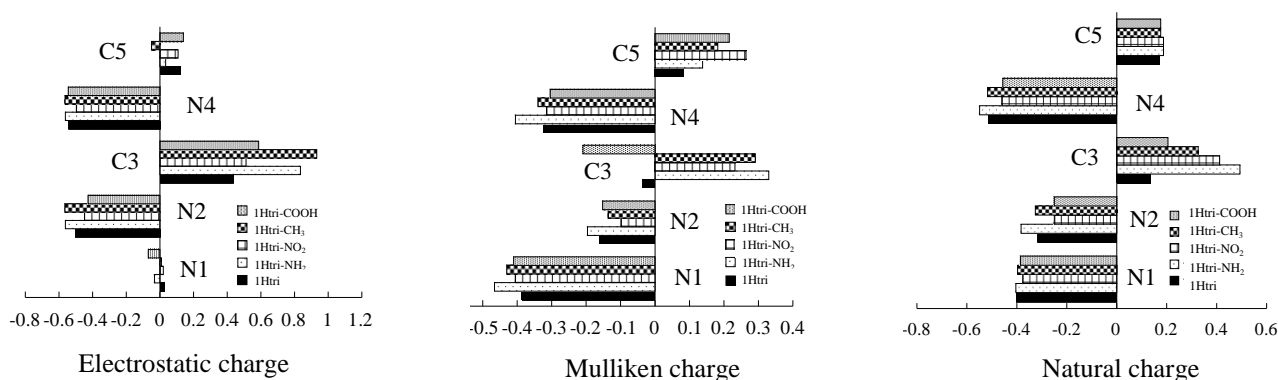


Fig. 4: Comparison of charge at each atom for electrostatic, Mulliken and natural charge.

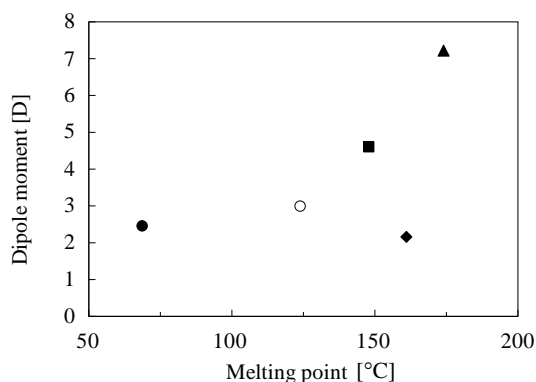


Fig. 5: Dipole moment versus melting point.

○1Htri, ◆1Htri-NH<sub>2</sub>, ▲1Htri-NO<sub>2</sub>, ●1Htri-CH<sub>3</sub>, ■1Htri-COOH

For the 1Htri coordinated with (-NO<sub>2</sub>), N2 and N4 became slightly positively charged with values of (-0.448) and (-0.497) for N2 and N4, respectively.

A comparison of the electrostatic, Mulliken and natural charge at each atom is shown in Fig. 4. There was no effect on electrostatic charge at N2 and N4 regardless of the electron-donating and electron-withdrawing substituents. For the coordinating substituents (-NH<sub>2</sub>), (-NO<sub>2</sub>), (-CH<sub>3</sub>) and (-COOH), C3 became more positively charged than 1Htri. There was no effect on electrostatic charge on N1. For the coordinating substituents (-NH<sub>2</sub>), (-NO<sub>2</sub>), (-CH<sub>3</sub>) and (-COOH), C5 became more positively charged than 1Htri. The coordinating electron-donating substituents (-NH<sub>2</sub>) and (-CH<sub>3</sub>) made C3 more positively charged than 1Htri. There was no effect on N1, N2, N4 and C5 and C3 became more positively charged than 1Htri for the natural charge.

## (2) dipole moment

The dipole moments of 1Htri and when coordinated with the substituent (-NH<sub>2</sub>), (-NO<sub>2</sub>), (-CH<sub>3</sub>) and (-COOH) are 2.96 [D], 2.16 [D], 7.22 [D], 2.43 [D] and 4.59 [D], respectively. The dipole moments versus melting point have a proportional relationship as shown in Fig. 5.

## (3) bond distance

The bond distance of 1Htri and its derivatives are summarized in Table 3. The bond distance of 1Htri at N1-N2 and C5-N1 is 1.357 [Å] and 1.352 [Å], respectively. For the electron-donating substituents (-NH<sub>2</sub>) and (-CH<sub>3</sub>), N1-N2 became longer and C5-N1 became shorter compared with 1Htri. For the electron-withdrawing substituents (-COOH) and (-NO<sub>2</sub>), N1-N2 became shorter and C5-N1 became longer than 1Htri.

The single bonds N1-N2, C3-N4 and C5-N1 are possible to be the cleavage bond. Therefore, degradation products of the lower molecules may be produced by disconnecting two single bonds at N1-N2 and C3-N4 or

C5-N1 and C3-N4 [10]. We consider that there is a relationship between bond distance and decomposition and assume that long bonds tend to become disconnected. The N1-N2 bond of 1Htri is longer than C5-N1 and it is therefore expected that 1Htri decomposes at N1-N2 and C3-N4. For the electron-donating substituents (-NH<sub>2</sub>) and (-CH<sub>3</sub>), decomposition is expected to occur at N1-N2 and C3-N4. For the electron-withdrawing substituents coordinating as (-COOH) and (-NO<sub>2</sub>), it is expected that decomposition will occur at C5-N1 and C3-N4.

Table 3: Summary of bond distance of 1Htri coordinated with substituent.

	Distance [Å]				
	N1-N2	N2=C3	C3-N4	N4=C5	C5-N1
1Htri	1.357	1.326	1.365	1.323	1.352
1Htri-NH <sub>2</sub>	1.369	1.331	1.369	1.323	1.346
1Htri-NO <sub>2</sub>	1.346	1.324	1.353	1.320	1.358
1Htri-CH <sub>3</sub>	1.358	1.330	1.371	1.322	1.350
1Htri-COOH	1.345	1.333	1.366	1.317	1.358

## 4. Conclusion

A study of the influence of substituent on the thermal decomposition of 1Htri was studied by SC-DSC. MO were used to study compound thermal and chemical properties. The  $T_{DSC}$  of the 1Htri coordinated with substituents was lower than that of the 1Htri. The  $\Delta E_a$  decreased when the 1Htri was coordinated with (-NH<sub>2</sub>), (-NO<sub>2</sub>), (-CH<sub>3</sub>) and (-COOH) substituents. 1Htri-NH<sub>2</sub> and 1Htri-CH<sub>3</sub> decompose at the N1-N2 and C3-N4 bonds, while 1Htri-COOH and 1Htri-NO<sub>2</sub> decompose at C5-N1 and C3-N4.

## 5. References

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