Article

Study on thermal behavior of 1H-1, 2, 4-triazole-copper complex with substituents

Wasana Kowhakul*†, Mieko Kumasaki**, and Mitsuru Arai*

*Environmental System course, Graduate School of Frontier Sciences, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, JAPAN
†corresponding author: wasana@explosion.chem.t.u-tokyo.ac.jp

**National Institute of Industrial Safety, 1-4-6 Umezono, Kiyose, Tokyo 204-0024, JAPAN

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Abstract

In this presented study, the effect of substituent, its ability to supply / withdraw electron to / from the reaction site, to 1H-1, 2, 4-triazole-copper complex (1Htri-Cu) were investigated. The substituents were selected from their Hammett constant value. Nitro group (-NO_2), Chloro group (-Cl) and Amino group (-NH_2) were selected and 1H-1, 2, 4-triazole-copper complex (1 Htri-Cu), Nitro-1H-1, 2, 4-triazole-copper complex [(1Htri- NO_2)Cu], Amino-1H-1, 2, 4-triazole-copper complex [(1Htri- NH_2)Cu] and Chloro-1H-1, 2, 4-triazole-copper complex [(1Htri-Cl)Cu] were synthesized and their thermal decomposition behaviors were investigated. According to Sealed Cell-Differential Scanning Calorimetry (SC-DSC), the substituents can be used to control the thermal stability of 1Htri-Cu complex by considering its Hammett constant value.

Moreover, in relation to the Flash pyrolysis / FTIR, the part of decomposed gases such as HCN, NO_2 and N_2 were similar at the 1000 degree Celsius. And finally, with the Gaussian03 calculation, T_{DSC} may concern with bond length of N_2-C_3.

Keywords: 1H-1, 2, 4-triazole, Metal complex, Substituent, Thermal decomposition, DSC

1. Introduction

Energetic materials are employed as gas generator in airbag because they easily release a large amount of decomposition gas, inflate an airbag, and protect passengers during life-threatening accidents. Many researchers have been attracted in developing new energetic materials for gas generators because of their practical use.

The important properties for gas generators are as following[1]: (1) Generate a large amount of decomposition gas in a short period, (2) No gas toxicity, (3) Low residue after decomposition, (4) High thermal stability, (5) Low sensitivity to physical stimulation such as mechanical impact, friction and static electricity, (6) Low cost, (8) No change in properties with time.

For the promising gas generators, high nitrogen contents are required from the standpoint of gas toxicity. If the substances with 100 % nitrogen percentage, Nitrogen-Clusters, were available (see Fig. 1), they would give clean gases when they decomposed. However, Nitrogen-Clusters only exist in theoretical calculation. Generally, the higher nitrogen percentage it has, the more unstable it is; there are only a few energetic materials whose nitrogen percentage is more than 50 %. Among those substances, Azole can not only give a large quantity of nitrogen gas but also have satisfactory stability[2]. Owing to high nitrogen content, they are used as gas generators.

In order to obtain better properties for gas generators, we have applied some chemical modifications to azole; we have designed in azole - metal complexes. Transition metals are commonly used to improve reaction rates for propellant because of their catalytic characteristics[3]. As a result, the response to stimuli becomes better.

Among myriad of triazole and transition metals, we chose 1H-1, 2, 4-triazole(1Htri) in this report which is the elementary structure of triazole (see Fig. 1). Copper was selected because of its catalytic characteristics[4), 5)].

On the other hand, over last 20 years, scientists and engineers have utilized various test methods on hundreds of chemicals to better understand chemical decompositions. The average decomposition characteristics, such as energy

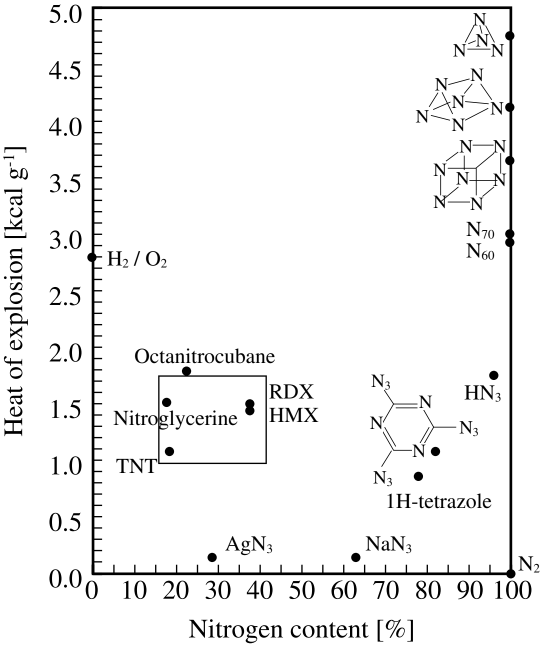

Fig. 1 Nitrogen content vs. heat of explosion.

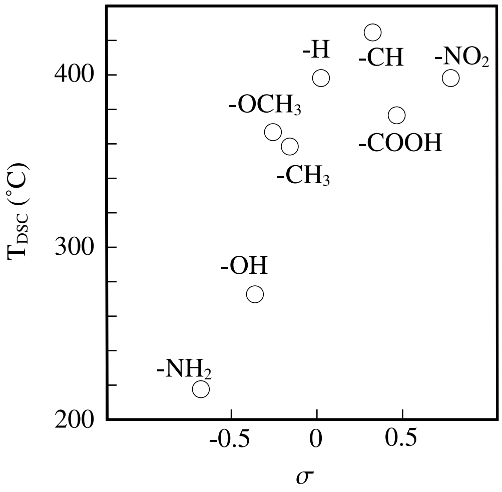

Fig. 2 Relationship between Hammett constant value (σ) and T_{DSC}.

of decomposition and decomposition onset temperature (T_{DSC}), were determined for chemical classes containing the following substituents : Nitro group ($-NO_2$), Chloro group (-Cl) and Amino group ($-NH_2$) etc.

Furthermore, the thermal behavior of Nitro-Benzene with various substituents has been investigated. T_{DSC} value was corresponding to their Hammett constant value (σ)[6]. When the Hammett constant were the positive value, T_{DSC} became higher and then the constants were the negative value T_{DSC} became lower too (see Fig. 2).

Therefore, this study suggested that the substituents can be used to control the thermal stability of Nitro-benzene. Consequently, the effect of substituent, which withdraw / donate electron from / to the reaction site, on the thermal behavior of 1Htri-Cu were investigated. In this study, Nitro group ($-NO_2$), Chloro group (-Cl) and Amino group ($-NH_2$) were selected as the substitutent because they have different the Hammett constant value (σ)[7] which indicate the degree of electron withdrawing or donating. 1Htri-Cu[8], [(1Htri- NO_2)Cu][9], [(1Htri-NH_2)Cu][9] and [(1Htri-Cu)Cl][10] were synthesized and their thermal behaviors were investigated. With this work, all complexes' thermal behaviors were studied by using Sealed Cell-Differential Scanning Calorimetry (SC-DSC) and then their thermal decomposed gas were analyzed by using Flash-pyrolysis / FT-IR. Finally, the structure of all complexes were performed by using Gaussian03 program as B3LYP / 6-31+G(d, p) basis.

2. Experiments

2.1 Samples

1Htri-Cu, [(1Htri-NO_2)Cu], [(1Htri-NH_2)Cu] and, [(1Htri-Cu)Cl] were synthesized following the previous studied and elemental analyses were carried out and compared with the literature value.

In relation to physical characterization, infrared spectra

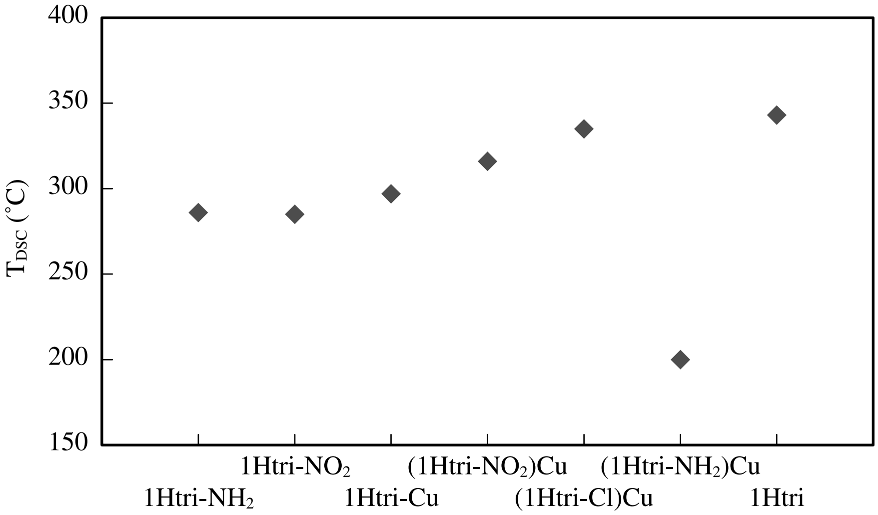

Fig. 3 1Htri with its complexes vs. T_{DSC}.

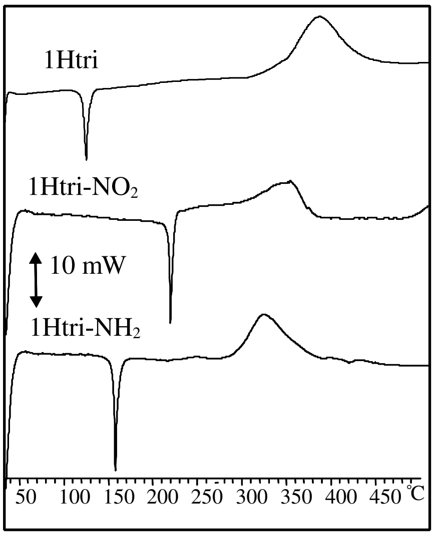

Fig. 4 SC-DSC curves of 1Htri and its substituents.

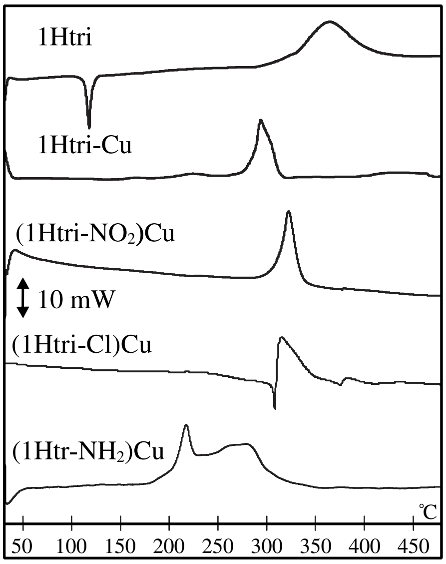

Fig. 5 SC-DSC curves of 1Htri and its complexes with substituents.

(4000 - 400 cm^{-1}) were recorded at room temperature. The samples were prepared using KBr technique. Moreover, NMR experiments were carried out by dissolving the complexes in Dimethyl Sulfoxide (DMSO) in 5 mm NMR tubes, and the ^{1}H spectra recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield™ MNR spectrometer.

2.2 SC-DSC thermal analysis

Sealed Cell-Differential Scanning Calorimeter (SC-DSC) was used for thermal analysis. SC-DSC was carried out using DSC20 with the operation system $STAR^{e}$ System (Mettler Toledo K. K.). In this study, stainless steel cells were selected as the high-pressure sample containers. The experiments were carried out at a heating rate of 10 K min^{-1} under a steady state flow of nitrogen (N_2). An almost constant sample mass of 1.0 mg was weighed. They were heated in the scanning mode from 30 °C to 500 °C. The temperature and heat flow calibrations were conducted by the recommended procedure using pure indium metal with a melting point of 429.6 K and heat of fusion of $\Delta Hf = 287.1$ J g^{-1}.

The SC-DSC data on the recording chart were analyzed as follows:

(1) The line connecting the point before the exothermic reaction starts and the point after it ends was used as the baseline.

(2) The temperature at which exothermic reaction starts (T_{DSC}) is determined from the intersection of the tangential line at the inflection point and the baseline.

2.3 Thermal decomposition products

Flash-pyrolysis was carried out in order to investigate the thermal decomposition products. The instrument was Pyroprobe 2000 and Brill cell (CDS Analytical Inc.) combined with a rapid-scan FT-IR spectrometer (MAGNA-IR 850, Nicolet Instrument Corporation). The starting and the ending temperatures were 30 °C and 1000 °C, respectively, with a heating rate of 10 K s^{-1}.The scanning resolution was 4 cm^{-1} and integration of the spectra was 4 times. The measuring time was 1 minute. The measurements were carried out less than 1 atm in a N_2 buffer gas.

2.4 Molecular orbital calculation

The quantum-chemical calculations were performed applying the Gaussian03 program as B3LYP / 6-31+G (d, p) basis. The geometry optimization providing also the molecule energies were followed by frequency calculation using the same basis set.

3. Results and discussion

3.1 SC-DSC

Figure 4 and 5 show SC-DSC curves of 1Htri, 1Htri-Cu, [(1Htri-NO_2)Cu], [(1Htri-NH_2)Cu], [(1Htri-Cl)Cu], 1Htri-NO_2 and 1Htri-NH_2 respectively. The value of T_{DSC} and Q_{DSC} are summarized in Table 2. Below its decomposition temperature, 1Htri exhibited endothermic peak that corresponded to melting while in case of the complexes, the endothermic peak disappeared. The phenomena might be due to the change of their electronic state[11].

While in case of 1Htri with the substituent such as -NO_2 and NH_2, T_{DSC} of both samples revealed almost the similar value (Table 1). The substituent effect on the thermal stability of the 1Htri-Cu complex was also investigated. From Table 2, T_{DSC} of [(1Htri-NO_2)Cu] and [(1Htri-Cl)Cu] were higher than that of 1Htri while T_{DSC} of [(1Htri-NH_2)Cu] was lower than that of 1Htri. Since these T_{DSC} of substituents-1Htri-Cu complexes tendency corresponded to their Hammett constant values (Table 3), -NO_2 and -Cl group were the positive value, the T_{DSC} were higher and NH_2 group was the negative so the T_{DSC} was lower. It can be considered that the T_{DSC} of 1Htri-Cu complex might be influenced by electronic state of the 1Htri ring with specific substituent. Therefore, this study suggested that the substituents can be used to control the thermal stability of 1Hti-copper complex.

Table 1 Summary of T_{DSC} of 1Htri and its substituents.

Sample	T_{DSC} (˚C)
1Htri	343
1Hti-NO_2	286
1Htri-NH_2	285

Table 2 Summary of T_{DSC} of 1Htri-Cu complexes.

Sample	T_{DSC} (˚C)
1Htri-Cu	297
(1Htri-NO_2) Cu	316
(1Hti-Cl) Cu	322
(1Htri-NH_2) Cu	200

Table 3 Hammett constant value.

Substituent	Hammett constant
-NO_2	0.78
-Cl	0.3
-NH_2	-0.66

Table 4 Various components of the decomposed gas at 1000 °C.

Sample	Product gases at 1000˚C
1Htri	N_2, CH_4, HCN
1Htri-Cu	CO_2, CO, N_2O, NO, HCN
(1Htri-NO_2) Cu	CO_2, CO, N_2O, NO, HCN
(1Htri-Cl) Cu	CO_2, CO, N_2O, NO, HCN
(1Htri-NH_2) Cu	CO_2, CO, N_2O, NO, HCN

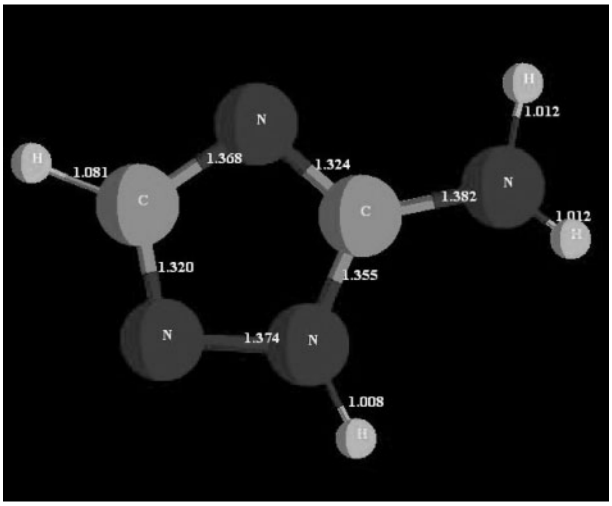

Fig. 6 1Htri-NH_2.

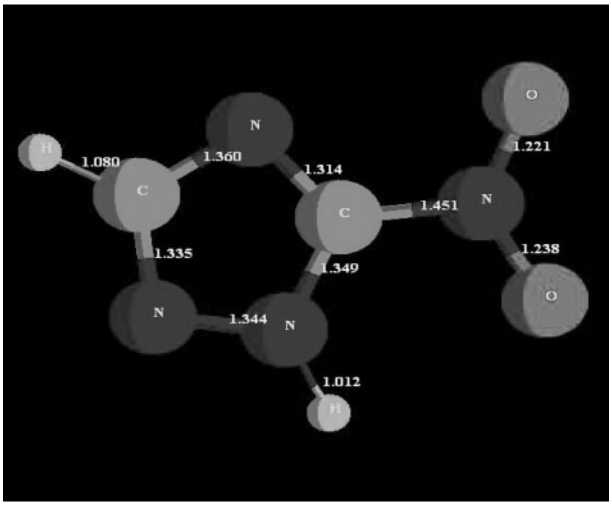

Fig. 7 1Htri-NO_2.

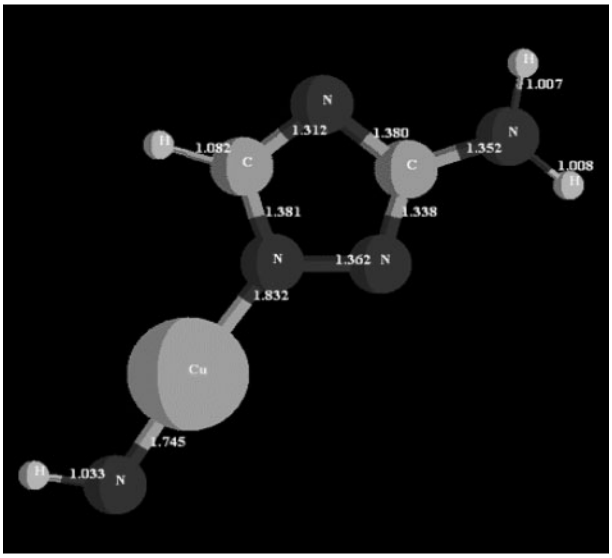

Fig. 8 (1Htri-NH_2) Cu.

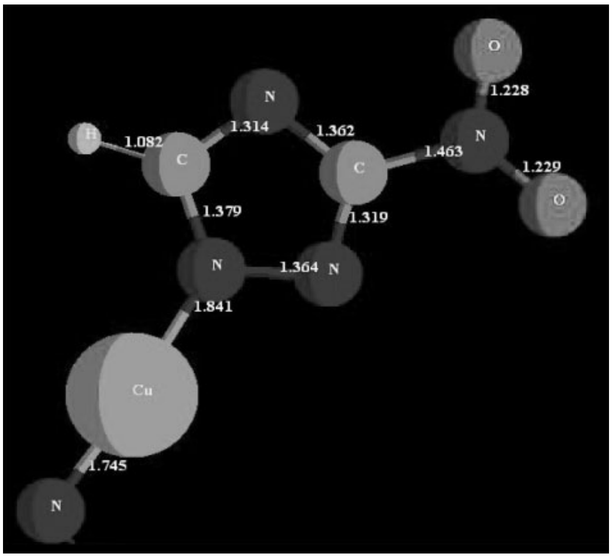

Fig. 9 (1Htri-NO_2) Cu.

3.2 Thermal decomposition products and molecular orbital calculation

Results of the Flash thermolysis / FT-IR tests of 1Htri, 1Htri-Cu, [(1Htri- NO_2)Cu], [(1Htri- NH_2)Cu] and [(1Htri-Cl)Cu] were shown in Table 4. The decomposition gas products were changed by the coordination of 1Htri to metal ions and substituent. Under the same conditions, 1Htri released N_2, CH_4 and HCN. In case of [(1Htri-NO_2)Cu], [(1Htri-NH_2)Cu] and [(1Htri-Cl)Cu] were CO_2, CO, N_2O NO HCN etc.

Moreover, the chemical structure of all samples which were evaluated by using Gaussain03 #B3LYP / 6-31 +G(d, p) basis (Table 5). The results from this work were compared with the experimental result and the previous studied[15]. It showed this studied calculation was almost nearly the real experimental result.

Table 5 Comparison of the X-ray experimental data with the Gaussian calculated data of 1Htri.

	Experimental	Calculated		
	X-ray[15]	HF[15]	B3P86[15]	B3LYP
		6-31G	6-311G	6-31+G
N1N2	1.354	1.363	1.346	1.357
N2C3	1.330	1.307	1.319	1.326
C3N4	1.353	1.371	1.358	1.365
N4C5	1.350	1.311	1.315	1.322
C5N1	1.344	1.343	1.346	1.352
N1N2C3	101.8	103.2	101.8	101.9
N2C3N4	114.5	113.5	115.3	115.2
C3N4C5	104.3	104.1	102.6	102.8
N4C5N1	107.1	109.4	109.8	109.8
C5N1N2	112.2	109.8	110.5	110.4

According to B3LYP / 6-31 +G(d, p), the 1Htri coordinate with substitutuent at position C3 atom (Fig. 6 ~ Fig. 9) all of bond length of 1Htri was changed. The summaries of the relationship between T_{DSC} and each bond length of 1Htri ring were showed as Fig. 10 ~ Fig. 14. Considering relationship between N2-C3 and T_{DSC} value might be the initial decomposition of 1Htri and 1Htri-complexes coordinated with substitutents.

The decomposition mechanisms of these complexes still required to consider the decomposed gas together.

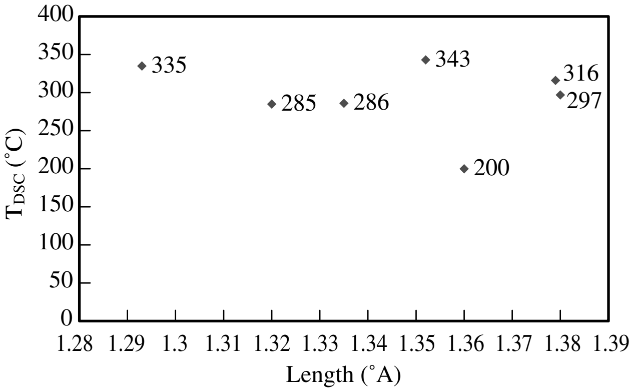

Fig. 10 N1-C5 bond length vs. T_{DSC}.

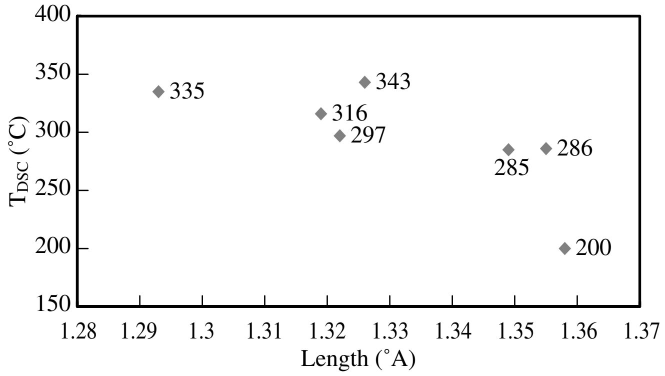

Fig. 11 N2-C3 bond length vs. T_{DSC}.

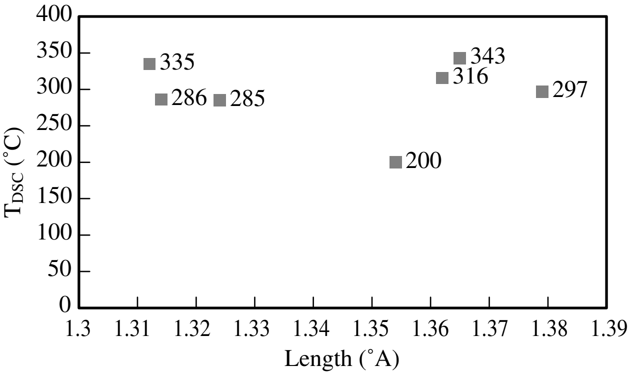

Fig. 12 C3-N4 bond length vs. T_{DSC}.

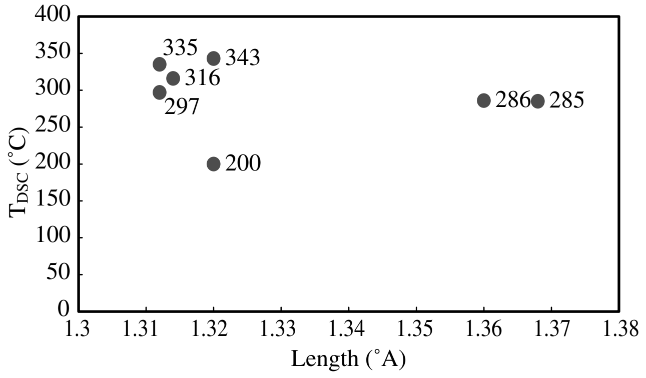

Fig. 13 C4-N5 bond length vs. T_{DSC}.

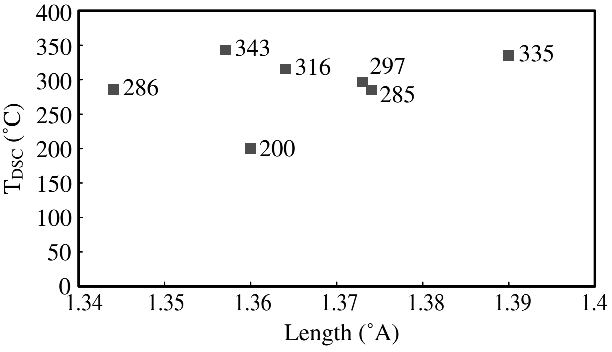

Fig. 14 N1-N2 bond length vs. T_{DSC}.

4. Conclusion

In order to study the effect of substituent in case of 1Htri-copper complex were investigated.

According to SC-DSC, the substituents can be used to control the thermal stability of 1Htri-Cu complex by considering its Hammett constant value.

According to the Flash pyrolysis / FTIR, part of decomposed gases such as HCN, NO_2, were similar at the 1000 degree Celsius and with B3LYP / 6-31 +G(d, p) basis calculation, T_{DSC} may concern with N_2-C_3.

As the above reasons, thermal analysis revealed azole with substituent and coordinated with copper was able to improve its thermal stability and thermal reactivity of pure triazole.

References

1) M. Tamura et al., Safety and Energetic Material, Asakura Shoten (*Japanese*) (1999).
2) M. Kumasaki et al., Kayaku Gakkaishi, 62(3), 109-116 (2001).
3) M. Akiyoshi et al., ibid., 62(4),161-167 (2001).
4) L. L. Garber and C. H. Brubaker, Journal of American Chemistry Society, 2518 (1968).
5) J. G. Haasnoot, Coordination Chemistry Reviews, 131-185 (2000).
6) M. Tamura, M. Arai and Y. Akutsu, Energetic Material and Safety, (*Japanese*) (1999).
7) Dean A. J., Lange`s handbook of chemistry, MgGraw-Hill Book company, 13th ed.
8) W. Kowhakul et al., Journal of Japan Explosives Society, 63(6), 362-366 (2002).
9) Kiuchi, Graduation thesis, The University of Tokyo, (2000).
10) Gabryszewski M., Polish journal of chemistry, 72(12), 2519-2523 (1998).
11) W. Kowhakul et al., The Proceeding of an Academic Meeting of Japan Explosive Soc. (autumn) (2004).
12) C. Carfacna et al., Thermochimica Acta, 37, 31-26 (1998).
13) Y. Mizushima et al., Journal of Japan Explosives Society, 39,124 (1978).
14) W. Kowhakul et al., Journal of Japan Explosives Society, (in press).
15) F. Billes et al., Journal of Molecular Structure (Theochem) 530, 183-200 (2000).