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ARTICLE in JOURNAL OF THERMAL ANALYSIS AND CALORIMETRY · OCTOBER 2014

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An experimental and theoretical study toward the synthesis, structure and thermal decomposition of some phenyl tetrazoles

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Received: 7 July 2014 / Accepted: 9 October 2014
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Abstract 1-phenyl-1H-tetrazole (**I**), 1(2-chlorophenyl)-1H-tetrazole (**II**), 1(4-chlorophenyl)-1H-tetrazole (**III**), 1(4-hydroxyphenyl)-1H-tetrazole (**IV**), 1(4-methoxyphenyl)-1H-tetrazole (**V**), 1(4-nitrophenyl)-1H-tetrazole (**VI**), 1(2-pyridyl)-1H-tetrazole (**VII**), and bis-1,4-tetrazol-1-yl benzene (**VIII**) were prepared from aniline, 2-chloro aniline, 4-chloro aniline, 4-hydroxy aniline, 4-methoxy aniline, 4-nitro aniline, 2-aminopyridine, and 1,4-phenyldiamine and characterized by Infrared spectroscopy, elemental analysis, mass spectrometry, ^1H Nuclear Magnetic Resonance, and ^{13}C Nuclear Magnetic Resonance spectroscopy. Suitable crystals of compounds **I**, **II**, **IV**, **V**, and **VI** were obtained and their molecular structures were determined using single crystal X-ray Diffraction. All tetrazole

compounds were also investigated using Thermogravimetry–Differential Thermal Analysis. At temperatures between 190–240 °C, the tetrazole ring decomposed exothermically. The decomposition products were estimated by relating the mass loss data and IR spectroscopy results of the residue with N_2 release and isonitrile formation as outcome of thermal decomposition. The heat of the exothermic decomposition was measured by Differential Scanning Calorimetry. Optimizations and frequency analyses of all tetrazole compounds were performed at the B3LYP/cc-pVDZ level of theory which are DFT-based structures. The optimum geometries of tetrazole compounds were enlightened with the help of Gaussian 09 pocket program. The enthalpies of formation for solid state were calculated theoretically by CBS-4 M algorithm. The calculated results were compared with the experimental data obtained from DSC study. It was seen that the enthalpies of decomposition of compounds **II**, **III**, **IV**, and **V** were in good agreement with the theoretical values. However, decomposition of compounds **I**, **VI**, **VII**, and **VIII** showed significant variation from the theoretical calculations.

Electronic supplementary material The online version of this article (doi:10.1007/s10973-014-4243-z) contains supplementary material, which is available to authorized users.

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Keywords Substituted-1H-tetrazoles · TG · DSC ·
Energetic materials · Thermal decomposition · CBS-4M

Introduction

Tetrazoles are nitrogen-rich stable materials that have been in literature since the 1880s [1–3]. Although they have been known for a long time, the number of studies focusing on tetrazoles has significantly increased in the last 20 years due to their interesting features. They can be used in pharmaceuticals, as synthetic building blocks in coordination chemistry, and as energetic materials. Due to the need of more energetic

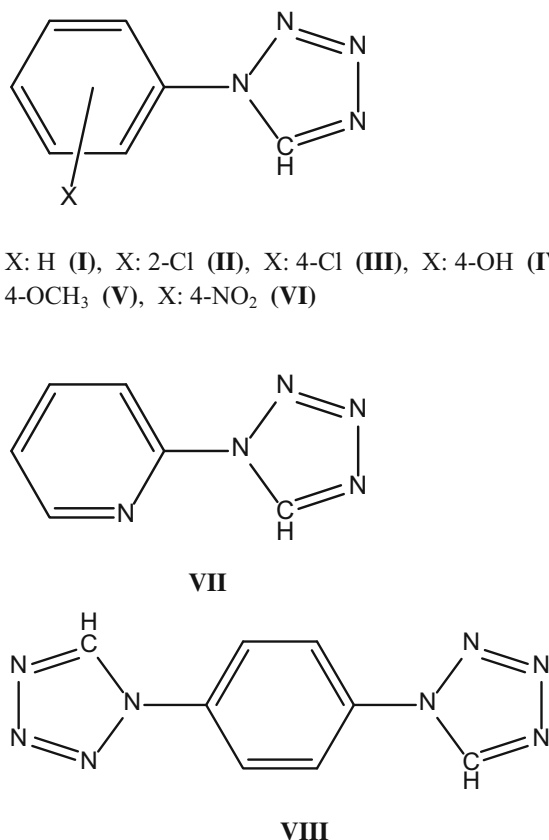


Fig. 1 Structures of synthesized tetrazoles

compounds with better stability and lower, nitrogen-rich chemistry is playing an important role in the development of pyrotechnics, propellants, and high explosives. In addition to the high nitrogen content, tetrazoles are commonly used substances for the production of environment-friendly energetic materials [4–9]. In literature, there are many studies about the synthesis of tetrazoles reported in recent years. Although the preparation methods are similar, it is better to divide them into two groups; 5-substituted tetrazoles synthesized from benzonitriles [10–19], and 1-substituted 1H-tetrazoles synthesized from primary amines [20–22]. Spectral characterizations of these tetrazole compounds have been reported, and there are only a few studies featuring thermal characterization and even fewer ones focusing on theoretical calculations.

In this study, eight 1-substituted 1H-tetrazole compounds were synthesized from substituted anilines and 2-aminopyridine, Fig. 1.

The compounds were characterized by IR spectroscopy, elemental analysis, mass spectrometry, and ^1H NMR and ^{13}C NMR spectroscopy. Suitable crystals of compounds **I**, **II**, **IV**, **V**, and **VI** were obtained and their molecular structures were determined using single crystal XRD followed by TG–DTA analysis.

Decomposition products were estimated with the help of mass loss data from TG study and m/z values from MS

study. Thermal decomposition was observed to begin with N_2 breaking away from the tetrazole ring. The molecular structures of prepared tetrazoles and possible reaction products were fully optimized without symmetry constraints at B3LYP/cc-pVDZ level of theory to C_1 symmetry in all cases and the frequencies were calculated at the same level of theory.

The standard formation enthalpies, free energy (G) of prepared tetrazoles and possible reaction products were calculated theoretically with Gaussian 09 software and CBS-4 M algorithm. The enthalpy of thermal decomposition reaction was determined from calculated formation enthalpies and the results were compared with the experimental findings of DSC.

Results and discussion

Compounds **I**, **II**, **IV**, **V**, and **VI** could be obtained as suitable single crystals for X-Ray analysis. So their cell data were obtained and molecular structures were determined in the light of the XRD output. The ORTEP drawings of these tetrazoles are given in Appendix A. XRD data and structure refinement for compounds **I**, **II**, **IV**, **V**, and **VI** are given in Appendix B; the selected bond angles and bond lengths obtained from the X-ray diffraction studies are given in Appendix C. As observed from Appendix A, all data were collected at 293 K. There are no abnormal stretching vibrations on any of the 5 molecules and refinement values were quite good. R values are 0.0365, 0.0353, 0.0373, 0.0542, and 0.0393. No abnormal bond length or angle values were detected (Appendix C).

All experimental values and literature entries are in correlation [5, 23]. The bond lengths, angles, and vibration of compounds **I**, **II**, **IV**, **V**, and **VI** were calculated using B3LYP and were optimized, and standard formation enthalpies and free energies (G) were calculated. The experimental and theoretical bond lengths around the tetrazole ring were found to be in agreement.

Some of the tetrazoles prepared in this study have recently been synthesized and their ^1H NMR, ^{13}C NMR data were reported [22]. However, NMR spectra were taken in CDCl_3 which makes the comparison possibly inaccurate since NMR data of the species of interest were recorded in d_6 -DMSO. The ppm values for CH proton in the tetrazole ring varies between $\delta = 9.91$ – 10.20 . Nevertheless, in the mentioned literature, the corresponding peak was observed earlier ($\delta = 8.92$ – 9.65). The solvent is highly responsible for the difference. The melting points given in the literature are compatible with our experimental findings with the exception of compound **VI**. The given melting point of compound **VI** is 199 – 200 °C but at this temperature, the species undergo thermal decomposition.

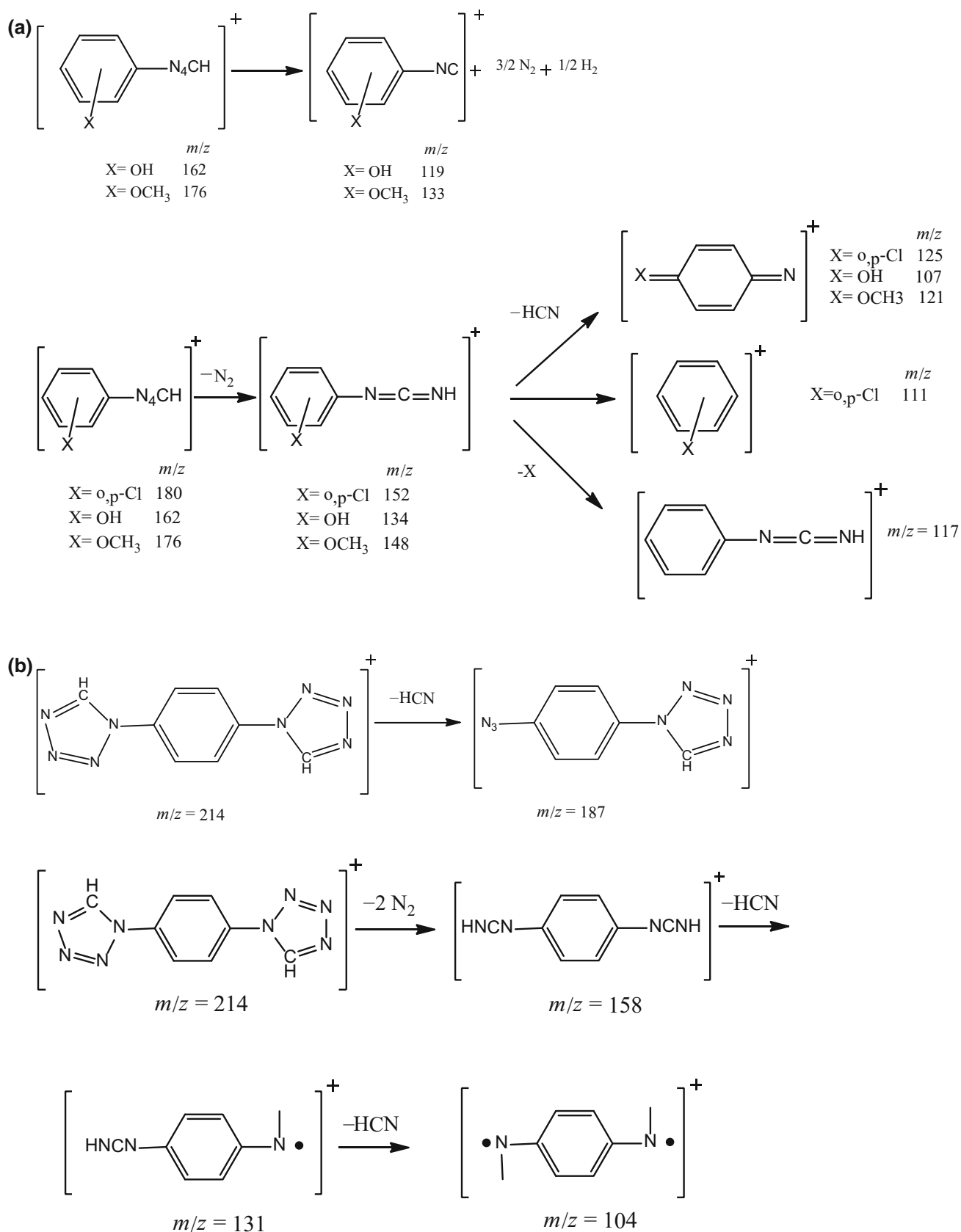


Fig. 2 **a** Observed fragmentation of tetrazoles **II**, **III**, **IV** and **V** at Mass spectrometer, **b** Mass fragmentation of compound **VIII**

Table 1 Thermoanalytic data of tetrazoles

Compound	Melting point/°C	Temperature interval/°C	Mass loss/%	
			Estimated/%	Experimental %
1-phenyl-1H-tetrazole (I)	64.95	170–224 DTA peak:218	29.45	56.20 ± 1.08
1(2-chlorophenyl)-1H-tetrazole (II)	89.04	159–210 DTA peak:191	23.82	29.47 ± 1.35
1(4-chlorophenyl)-1H-tetrazole (III)	161.02	178–210 DTA peak:204	23.82	25.35 ± 0.84
1(4-hydroxyphenyl)-1H-tetrazole (IV)	–	208–243 DTA peak:236	26.54	28.03 ± 1.02
1(4-methoxyphenyl)-1H-tetrazole (V)	119.30	176–213 DTA peak:208	24.43	26.74 ± 1.74
1(4-nitrophenyl)-1H-tetrazole (VI)	–	194–228 DTA peak:213	22.51	57.65 ± 2.46
1(2-pyridyl)-1H-tetrazole (VII)	126.34	152–210 DTA peak:205	29.25	30.32 ± 0.82
Bis-1,4-tetrazol-1-yl benzene (VIII)	–	211–237 DTA peak:230	40.19	94.34 ± 2.14

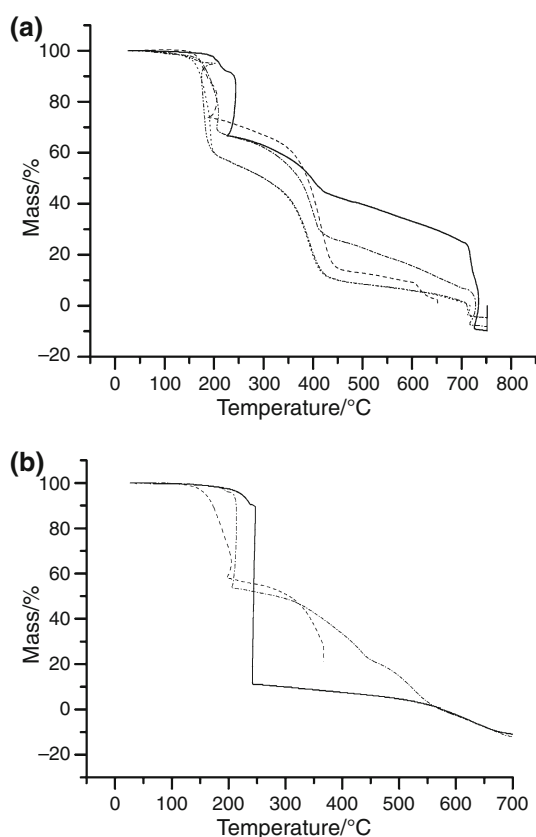


Fig. 3 **a** The TG curves of dotted–compound **II**; dashed–compound **III**; solid–compound **IV**; dot-dashed– compound **V**; dot-dot-dashed compound **VII**, **b** The TG curves of dashed–compound **I**; dot-dashed–compound **VI**; solid– compound **VIII**

When m/z values of fragments in the mass spectra are examined, it is estimated that two fragments occur after N_2 and an H_2 departs from the molecular peak. Other fragments vary depending on the substituent.

On the other hand, in the mass spectrum of Bis-1,4-1H-tetrazole-1-yl-benzene, similar peaks were observed corresponding to two N_2 and two HCN fragments Fig. 2b.

All prepared tetrazoles have also been investigated using thermogravimetry. In every case, exothermic reactions are observed. Thermoanalytic data of the tetrazoles are given in Table 1. For their respective thermal decomposition reactions, mass loss of compounds **II**, **III**, **IV**, **V**, and **VII** were in the range of 26–30 % whereas the mass loss of compounds **I**, **VI**, and **VIII** were greater than 50 %. The TG curves of all species are shown in Fig. 3a, b and the DSC curves in Fig. 4a, b.

Computational calculation steps

The molecular structures of tetrazoles **I–VIII** were fully optimized without symmetry constraints at B3LYP/cc-pVDZ level of theory to C_1 symmetry in all cases and the frequencies were calculated at the same level of theory and compared with the experimental values. Optimized molecular structure of 1(2-chlorophenyl)-1H-tetrazole (**II**), 1(4-chlorophenyl)-1H-tetrazole (**III**), 1(4-hydroxyphenyl)-1H-tetrazole (**IV**), 1(4-methoxyphenyl)-1H-tetrazole (**V**), 2-chlorophenyl-isonitrile (**IX**), 4-chlorophenyl-isonitrile (**X**), 4-hydroxyphenyl- isonitrile (**XI**), and 4-methoxyphenyl- isonitrile (**XII**) are shown in Appendix D.

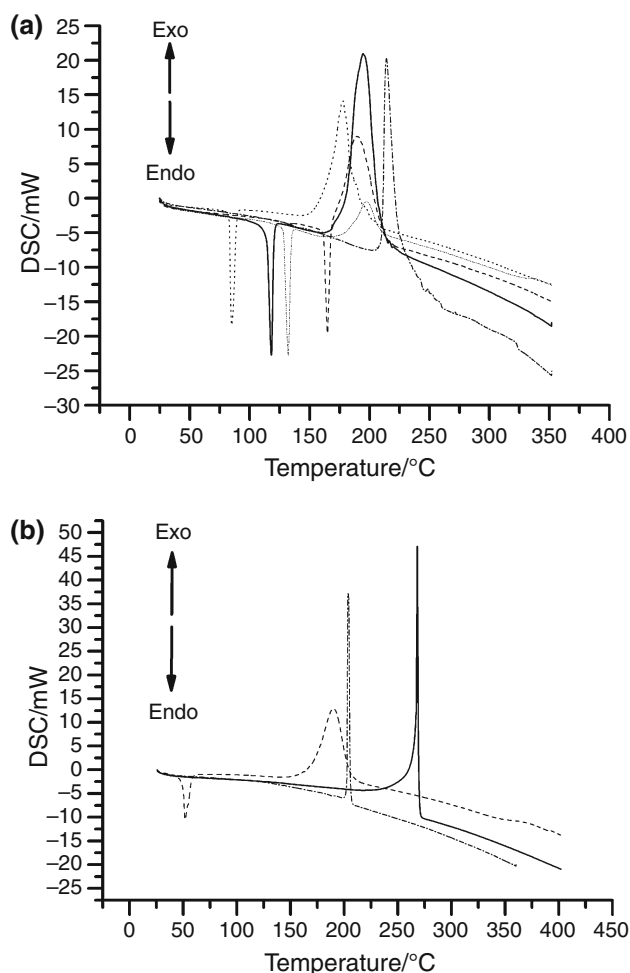


Fig. 4 **a** The DSC curves of dotted–compound **II**; dashed–compound **III**; dot-dashed–compound **V**; solid–compound **IV**; dot-dot-dashed compound **VII**, **b** The DSC curves of dashed– compound **I**; dot-dashed–compound **VI**; solid–compound **VIII**

The enthalpies of the gas-phase species **M** were computed according to the atomization energy method (Eq. (1); Tables 2, 3) [24–26]. In Eq. 1, $\Delta_f H^\circ(\text{g}, \text{M})$ stands for the gas-phase enthalpy of for $H(\text{M})$ represents the CBS-4 M calculated mation of the molecule, **M**, under investigation; enthalpy of the molecule **M** (H_{298} in Table 2);

$\Sigma_{\text{atoms}} H^\circ$ denotes the CBS-4 M calculated enthalpies for the individual atoms (Table 2), and $\Sigma_{\text{atoms}} \Delta_f H^\circ$ stands for the experimentally reported literature values for the enthalpies of formation for the corresponding atoms ($\Delta_f H^\circ_{298}$ in Appendix E). The atomic $\Delta_f H^\circ_{298}$ values were received as 217,99 for hydrogen, 716,72 for carbon, 472,79 for nitrogen, 249,37 for oxygen, and 120,92 for chloride as kJ mol^{-1} [27].

$$\Delta_f H^\circ_{(\text{g}, \text{M})} = H_{(\text{M})} - \Sigma H^\circ + \Sigma \Delta_f H^\circ \quad (1)$$

The enthalpies of sublimation for all tetrazoles and approximated decomposition products were estimated

Table 2 CBS-4 M Results

Compound	Point group ^a	NIMAG ^b	$-H^{298}/\text{a.u.}^c$	$-G^{298}/\text{a.u.}^d$
II	C ₁	0	947.73	947.77
III	C ₁	0	947.73	947.77
IV	C ₁	0	563.73	563.77
V	C ₁	0	602.95	602.99
VIII	C ₁	0	745.31	745.36
IX	C ₁	0	783.09	783.13
X	C ₁	0	783.09	783.13
XI	C ₁	0	399.09	399.13
XII	C ₁	0	438.31	438.35
H		0	0.50	0.51
C		0	37.79	37.80
N		0	54.52	54.54
O		0	74.99	75.01
Cl		0	459.67	459.69

^a Point group

^b Number of imaginary frequencies

^c CBS-4 M calculated enthalpy

^d CBS-4 M calculated free energy

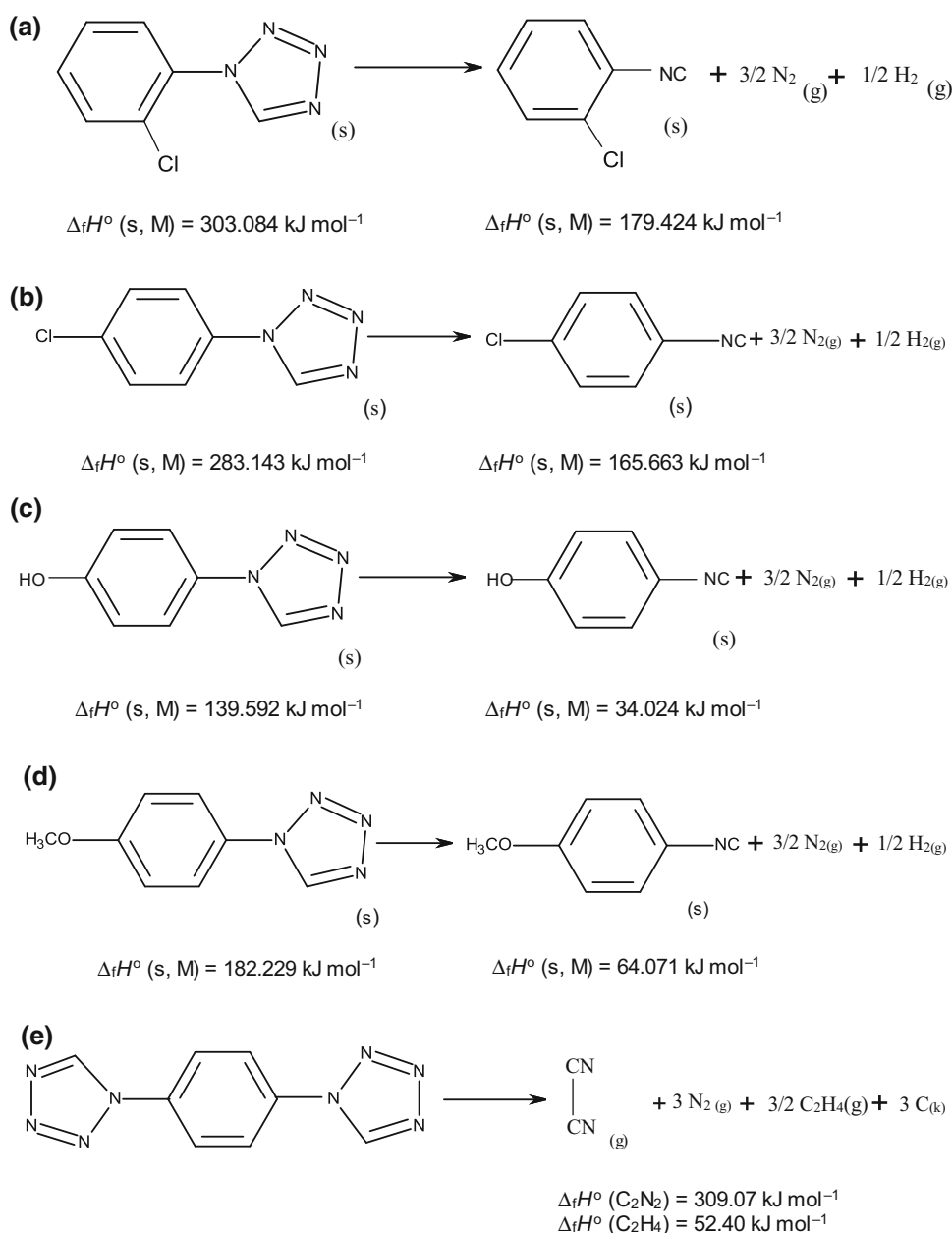
Table 3 Enthalpies of the gas-phase species **M**, Enthalpies of Sublimation (ΔH_{sub}), and Enthalpies of Formation ($\Delta_f H^\circ$) of the Compounds

Compound	$\Delta_f H^\circ(\text{g}, \text{M})/\text{kJ mol}^{-1}$	$\Delta H_{\text{sub}}/\text{kJ mol}^{-1}$	$\Delta_f H^\circ(\text{s}, \text{M})/\text{kJ mol}^{-1}$
II	371.29	68.21	303.08
III	365.49	283.14	283.14
IV	235.34	95.74	138.90
V	255.98	182.23	182.23
VIII	772.38	182.23	675.36
IX	234.88	55.46	179.42
X	230.71	65.05	165.66
XI	102.27	68.24	34.03
XII	122.35	58.28	64.07

Table 4 The comparison of theoretical reaction enthalpies and experimental results of DSC, concerning the reactions given in Fig. 5

	Experimental results/ kJ mol^{-1}	Theoretical results/ kJ mol^{-1}
II	-119.83 ± 3.79	-123.66 (6 a)
III	-126.22 ± 0.93	-117.48 (6 b)
IV	-140.16 ± 21.56	-105.57 (6 c)
V	-163.58 ± 12.68	-118.16 (6 d)
VIII	-243.76 ± 27.94	-287.69 (6 e)

according to Trouton's law (Eq. 2) with observed melting points from the TG curves, 64.8, 89.8, 165.0, 240.0, 119.2, 215.0, 130.2, and 243.0 °C, respectively. The validity of Trouton's law reflects the fact that the entropy of

Fig. 5 Probable thermal decomposition reactions

vaporization is approximately constant for many compounds and that $\Delta H_{\text{sub.}} \approx \Delta H_{\text{vap.}} + \Delta H_{\text{fusion}}$, with $\Delta H_{\text{vap}} \gg \Delta H_{\text{fusion}}$ so that $\Delta H_{\text{sub.}} \approx \Delta H_{\text{vap.}}$

$$\Delta H_{\text{sub.}} = 188 T_m \text{ J mol}^{-1} \quad (2)$$

The calculated molar enthalpies of formation for all tetrazoles and their approximated decomposition products are summarized in Appendix E and the calculated and experimental enthalpies of decomposition have been compared in Table 4.

In Fig. 3a the thermal behavior of 2-chloro, 4-chloro, 4-hydroxy, 4-methoxy phenyl, and 2-pyridyl tetrazoles are seen. The mass loss values approximately correspond to the

detachment of $3/2 \text{ N}_2 + 1/2 \text{ H}_2$ from the tetrazole ring. In this manner, the residue should be a 2 or 4 substituted isonitrile, Fig. 5.

The mass spectra give an idea for a possible explanation of this phenomenon. It is likely to obtain an isonitrile molecule if a nitrogen molecule or $3/2 \text{ N}_2 + 1/2 \text{ H}_2$ molecule breaks away from any tetrazole structure.

The m/z values observed near the molecular peaks in the mass spectra belong to the ion peaks of the mentioned molecules Fig. 2a, b. On the other hand, mass loss is much higher in the thermal decompositions of 1-phenyl-1H-tetrazole (56,20 %), 1(4-nitrophenyl)-1H-tetrazole (57 %), and bis-1,4-1H-tetrazole-1-yl benzene (95 %).

In these cases, the mass loss is even larger than the mass of whole tetrazole ring. In order to explain these results, theoretical software was used for quantitative analysis purposes. In this manner, Gaussian 09 was employed for calculation of the formation enthalpies of the reactants and products given in Fig. 5. Afterward, these theoretical formation enthalpies were used to determine the theoretical reaction enthalpy following the Hess' Law [28].

Table 4 shows the theoretical reaction enthalpies for the given species as well as the experimental findings from DSC study for comparison. Reaction enthalpy data dealing with the materials synthesized in this study is absent in the literature but there are entries involving 5-substituted tetrazoles [4]. Also, a theoretical study about the change in activation energy with varying substitutes has been noted. In that study, the activation energies of 1- and 5-substituted tetrazoles were calculated with DFT-B3LYP method and MP3 algorithms [29]. Again, the results seem to be parallel to our findings. For the tetrazole compounds given in Fig. 3a, the experimental and theoretical values are comparable with each other. On the other hand, Fig. 3b shows an unexpectedly large mass loss. For these tetrazoles, the experimental results are considerably different than the theoretical calculations according to the expected reactions given in Fig. 5.

It is obvious in both theory and TG results that the expected products did not occur. 2-chloro, 4-chloro, 4-hydroxy, and 4-methoxy substituted compounds yielded results where theory and experiment converged. This agreement may be due to the possibility of quinoid structure formation. 2-chloro substituted tetrazoles tend to form orthoquinones, whereas 4-chloro, hydroxy, or methoxy substituted tetrazoles tend to form paraquinones. The stability of quinoid structures stops the decomposition of the molecule at this level.

Nevertheless, such a formation is unlikely in 1-phenyl-1H-tetrazole. This leads to a major thermal decomposition. 1(4-nitrophenyl)-1H-tetrazole does possess the ability to form a quinone but the effect of the nitro group in the molecule leads to a larger mass loss. Assuming the cleavage of $3\text{N}_2 + \text{H}_2$ from the two tetrazole rings of Bis-1,4-1H-tetrazole-1-yl benzene, the product should be benzene di-isonitrile.

Under these circumstances, theoretical calculation yields a completely different result than the DSC experiment. Since the mass loss is 95 %, it is quite likely that this molecule decomposes in a different way. Indeed, the theoretical result converges to the experimental finding if the decomposition is assumed to be going on as given in Fig. 5.

The highlight here should be if that the theoretical software can be used for analytical purposes. Although in our case, it was not possible to estimate the thermal decomposition products of compound **VIII**, the software

has proven to be quite useful in estimations for compounds **II**, **III**, **IV**, and **V**. Therefore, this study supports the fact that theoretical calculation software can be used for analytical determinations and estimations.

Conclusions

- Restating what has been done in this study, eight tetrazole compounds were synthesized from substituted anilines, azide ion, and triethyl orthoformate in acetic acid, these tetrazoles were first characterized by means of IR, ^1H NMR ve ^{13}C NMR spectroscopy and investigated by TG-DTA. Molecular models of **I**, **II**, **IV**, **V**, and **VI** tetrazole compounds were determined by evaluating their XRD characteristics.
- The molecular structure and frequency of all tetrazole compounds and decomposition products optimized were calculated at B3LYP/cc-pVDZ level of theory. Experimental and theoretical bond lengths and bond angles around tetrazole ring of compounds **I**, **II**, **IV**, **V**, and **VI** were found to be in agreement with their X-ray counterparts. Calculated frequencies of all tetrazole compounds were in accordance with the observed IR spectra.
- The theoretical formation enthalpies of the reactants and decomposition products were calculated using CBS-4M running under Gaussian 09 software package. Enthalpy of tetrazole compounds **II**, **III**, **IV**, **V** and thermal decomposition reaction was compatible with experimental findings of DSC.
- The mass loss results of thermogravimetric investigation, that o- and p- substituted chloro, hydroxy, and methoxy-phenyl tetrazoles decompose by yielding $3/2$ mol of $\text{N}_{2(\text{g})}$ and $1/2$ mol of $\text{H}_{2(\text{g})}$. This strengthens the electron delocalization and the direction of the explosion mechanism of isonitrile.
- It was observed that non-substituted phenyl containing tetrazoles and the nitrophenyl containing one did not decompose in the expected way. Because NO_2 substitute group in the benzene ring was reduced, the electron delocalization was higher than the mass loss. As a group which increases the ring electron delocalization is not situated on phenyl tetrazole, only a benzyl ring remains after destruction of the tetrazole compound. This result is supported through the IR spectrums. The dual nature of bis-tetrazole increases the ring instability leading to degradation with 95 % mass loss. Increase of the nitrogen atoms leads to a higher reaction enthalpy.
- Then the reaction enthalpies were calculated simply by using Hess' law. The experimental results were found to be close to the theoretical values in decompositions

of o- and p- substituted phenyl tetrazoles. We will continue to work to determine the decomposed product of this tetrazole compounds.

Acknowledgements Financial support of this work by the University of Ankara Scientific Research Fund under contract no. 12B4240003 and Ahi Evran University Scientific Research Fund under contract no. 4001.12.014 are gratefully acknowledged. We are indebted to and thank Prof. Dr. Wolfgang Donner for providing laboratory facilities at TU Darmstadt.

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