

# Synthesis, Characterization, and Energetic Properties of Diazido Heteroaromatic High-Nitrogen C–N Compound

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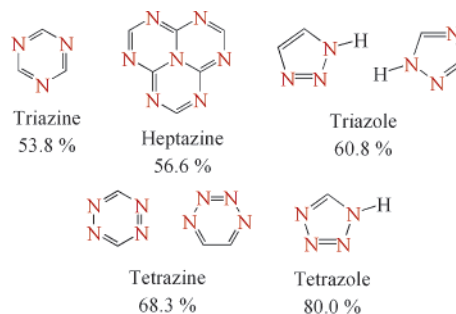
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**Abstract:** The synthesis, characterization, and energetic properties of diazido heteroaromatic high-nitrogen C–N compound, 3,6-diazido-1,2,4,5-tetrazine (DiAT), are reported. Its normalized heat of formation ( $N\Delta H_f^\circ$ ), experimentally determined using an additive method, is shown to be the highest positive  $N\Delta H_f^\circ$  compared to all other organic molecules. The unexpected azido-tetrazolo tautomerizations and irreversible tetrazolo transformation of DiAT are remarkable compared to all other polyazido heteroaromatic high-nitrogen C–N compounds, for example, 2,4,6-triazido-1,3,5-triazine; 4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine; 4,4',6,6'-tetra(azido)azo-1,3,5-triazine; and 2,5,8-tri(azido)-1,3,4,6,7,9,9b-heptaazaphenalene (heptazine).

## Introduction

Energetic organic compounds with high-nitrogen content<sup>1,2</sup> have currently attracted significant attention from many researchers because of their novel properties, for example, high density,<sup>3,4</sup> high positive heat of formation ( $+\Delta H_f^\circ$ ),<sup>5–7</sup> and high thermal stability,<sup>8–10</sup> that result in numerous unique applications including effective precursors for carbon nanospheres<sup>11,12</sup> and carbon nitride nanomaterials,<sup>13–16</sup> solid fuels in micropropulsion systems,<sup>17,18</sup> gas generators,<sup>19</sup> smoke-free pyrotechnic fuels,<sup>20,21</sup> and fire extinguishers onboard military aircraft.<sup>22,23</sup> These high-

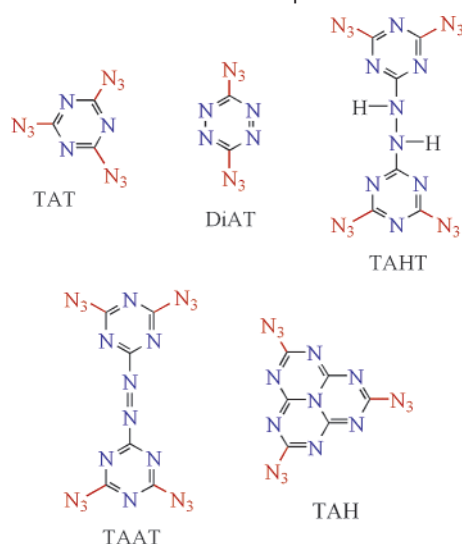
**Scheme 1.** C–N Heteroaromatic High-Nitrogen Compounds



nitrogen compounds form a unique class of C–N heteroaromatic compounds, for example, triazine,<sup>24</sup> heptazine,<sup>25–27</sup> triazole,<sup>28–31</sup> tetrazine,<sup>32,33</sup> and tetrazole,<sup>34</sup> Scheme 1.

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**Scheme 2.** Azido Heteroaromatic Compounds

In particular, polyazido heteroaromatic compounds have recently been extensively studied for their useful applications either in material science<sup>35,36</sup> or as high-density energetic materials.<sup>3,4</sup> In 1963, Marcus reported the preparation of 3,6-di(azido)-1,2,4,5-tetrazine (DiAT) with its melting point of 130 °C; however, no other physical properties or crystal structure were available.<sup>37</sup>

As part of our continual effort in high-nitrogen energetic materials, we herein report on an improved synthetic pathway for DiAT and its full detailed characterization. Its unexpected azido-tetrazolo tautomerizations and irreversible tetrazolo transformation are also described. From our characterization and property data, DiAT possesses the highest positive normalized heat of formation ( $N\Delta H_f = \Delta H_f$  divided by the number of atoms in a molecule), that was experimentally determined using an additive method, compared to all other organic molecules. As shown in Scheme 2, it is remarkable that neither 2,4,6-tris(azido)-1,3,5-triazine (TAT);<sup>38</sup> 4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine (TAHT);<sup>5,8</sup> 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT);<sup>5,8</sup> nor 2,5,8-tris(azido)-s-heptazine (TAH)<sup>16</sup> has been reported to undergo azido-tetrazolo tautomerization and tetrazolo transformation.

## Experimental Section

The compounds appearing in this study are shown in Scheme 3.

3,6-Bis(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**1**); 3-hydrazino-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**2**); 3,6-di(hydrazino)-1,2,4,5-tetrazine (**3**); 3-amino-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**4**); 3,6-di(amino)-1,2,4,5-tetrazine (**5**); 3-azido-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**6**); 2,3-(tetrazolo)-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (**6A**); 3,6-di(azido)-1,2,4,5-tetrazine (**7**); 3-azido-1,6-(tetrazolo)-1,2,4,5-tetrazine (**7A**); 1,6:2,3-bis(tetrazolo)-1,2,4,5-tetrazine (**7B**).

Abbreviations and formulas used in the text include the following: TBAH =  $[Bu_4N]PF_6$  = tetrabutylammonium hexafluorophosphate and DMP = 3,5-dimethylpyrazol-1-yl.

**Materials.** House water was purified with a Barnstead E-Pure deionization system. High-purity acetonitrile, chloroform, methylene chloride, tetrahydrofuran, dimethylformamide, and dimethyl sulfoxide were used as received from Aldrich. Hydrazine hydrate and sodium nitrite were purchased from Fisher and were used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were used as received. TBAH was recrystallized three times from boiling ethanol and was dried under vacuum at 120° for 2 days. Other chemicals employed in the preparation of compounds were reagent grade and were used without further purification.

**Instrumentation and Measurement.** Electronic absorption spectra were acquired by using a Hewlett-Packard Model 8453 diode array UV–visible spectrophotometer in quartz cuvettes. Elemental analyses were performed by Atlantic Microlabs (Norcross, GA) and Los Alamos National Laboratory. FT-IR spectra were recorded on a Nexus 670 FT-IR spectrophotometer at 4  $cm^{-1}$  resolution interfaced with an IBM-compatible PC. IR measurements were made in Nujol mulls.  $^1H$  NMR and  $^{13}C$  NMR spectra were obtained in  $DMSO-d_6$ ,  $CD_3CN$ ,  $(CD_3)_2CO$ ,  $CD_3OD$ , and  $CDCl_3$  recorded on a JEOL Eclipse 300 Fourier transform spectrometer. Melting points were determined by differential scanning calorimetry (DSC Exo.) at 5 °C/min using TA instruments 2920 Modulated DSC. Heats of formation ( $\Delta H_f$ ) were measured using a Parr Adiabatic Calorimeter model 1720. All reported values are the average of at least three independent experiments and are within  $\pm 2$  kJ/mol.

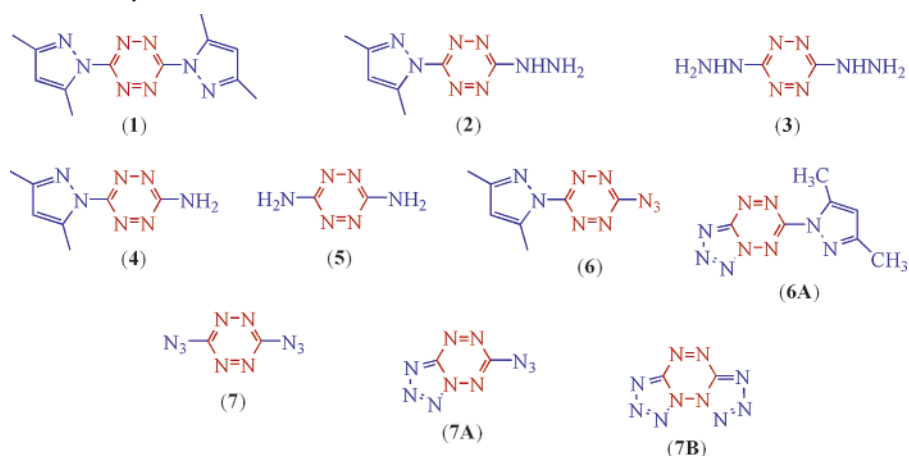
Cyclic voltammetric experiments were carried out at scan rates 100, 200, 400, and 800 mV/s with the use of a PAR model 263 potentiostat. All measurements were conducted in a three-compartment cell in chloroform and dimethyl sulfoxide with 0.2 M TBAH as the supporting electrolyte. A 1.0-mm platinum-working electrode was used for these measurements. All potentials are referenced to the saturated sodium chloride calomel electrode (SSCE, 0.236 V versus NHE) at room temperature and at 80 °C and are uncorrected for junction potentials. In all cases, the auxiliary electrode was a platinum wire. The solution in the working compartment was deoxygenated by  $N_2$  bubbling. All redox potentials are the average of at least three independent experiments and are within  $\pm 2$  mV. Los Alamos is at the elevation of 7500 ft and atmospheric pressure of 580 Torr (11.2 psi or 0.76 atm). Humidity is normally below 20% during spring.

**Synthesis and Characterization.** Since **7** is extremely sensitive to friction, electrostatic discharge, and impact,<sup>39</sup> one should always handle **7** wet, use thick gloves behind a blast shield, and limit the amount to less than 300 mg. Compounds **1**,<sup>40</sup> **2**,<sup>41</sup> **3**,<sup>41,42</sup> **4**,<sup>40</sup> and **5**<sup>40</sup> were prepared by literature procedures.

**3-Azido-6-(3,5-dimethylpyrazol-1-yl)-1,2,4,5-tetrazine (6).** To a 100-mL-jacketed beaker containing 40 mL of 3 M HCl was added 2.06 g (10 mmol) of **2**, and the suspension was stirred until complete dissolution occurred. The temperature was adjusted to  $-5$  °C, while a solution of  $NaNO_2$  (0.76 g, 11 mmol) in 10 mL of water was added dropwise with vigorous stirring while maintaining the temperature below 3 °C. The solution was then extracted four times with 50 mL 75:25 (v/v) *tert*-butylmethyl ether:hexane mixture. The combined organic layer was dried with  $Na_2SO_4$  and was concentrated to give **6** as a low melting orange solid (80 °C), yield 1.6 g (75%). Caution: although **6** does not possess any sensitivity problems, care should always be taken when working with compounds containing azide, for example, gently transfer the compound using plastic spatulas.  $^1H$  NMR ( $CDCl_3$ )  $\delta$  2.23 (s, 3H), 2.54 (s, 3H), 6.05 (s, 1H);  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  13.18, 13.94, 111.80, 143.68, 154.53, 159.34, 164.46. Anal. calcd for  $C_6H_2N_9$ : C, 38.71; H, 3.25; N, 58.04. Found: C, 38.85; H, 3.36; N, 57.88.

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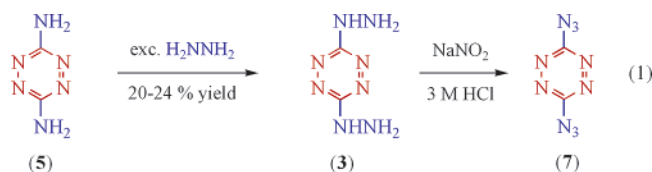
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**Scheme 3.** Compounds in the Study

**3,6-Di(azido)-1,2,4,5-tetrazine (7).** To a 100-mL-jacketed beaker containing 40 mL of 3 M HCl was added 0.5 g (3.52 mmol) of **3**, and the suspension was stirred until complete dissolution occurred. The temperature was adjusted to  $-5^{\circ}\text{C}$ , while a solution of  $\text{NaNO}_2$  (0.61 g, 8.84 mmol) in 10 mL of water was added dropwise with vigorous stirring while maintaining the temperature below  $3^{\circ}\text{C}$ . The reaction was allowed to proceed at  $0^{\circ}\text{C}$  for 30 min during which time a bright orange solid precipitated. It was filtered using a Büchner funnel, washed thoroughly with cold water, and air-dried. Without isolation, this crude product was washed into a plastic beaker with methylene chloride or chloroform leaving an insoluble impurity behind. The filtrate was slowly evaporated to give a crystalline product in a 54% yield. Caution: **7** is extremely sensitive to spark, friction, and impact! The material should be gently handled with plastic spatulas. Grounding straps, thick gloves, and face shield should be used at all times. This reaction should be done inside a hood and behind a thick blast shield. Differential scanning calorimetry (DSC Exo.): onset of decomposition at  $130^{\circ}\text{C}$ ;  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ): 164.2 ppm; IR (Nujol mull):  $\nu(\text{N}_3)$  2169 (vs) and 2142 (vs);  $\nu(\text{tetrazine})$  1460 (vs), 1193 (vs), 1065 (vs), 927 (vs), 817 (vs), 546 (vs)  $\text{cm}^{-1}$ ; UV–vis ( $\text{CHCl}_3$ ) ( $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 541 sh ( $4.64 \times 10^3$ ), 521 ( $6.50 \times 10^3$ ), 373 ( $1.79 \times 10^3$ ), and 268 ( $1.94 \times 10^4$ ). Cyclic voltammetry in 0.2 M  $\text{Bu}_4\text{NPF}_6/\text{CHCl}_3$  (V vs SSCE):  $E_{1/2} = +0.518\text{ V}$ . Because of its extreme sensitivity, elemental analysis was not performed. Two azido substituents on the tetrazine parent ring have made **7** to be a primary explosive. Its explosive sensitivities are (1) friction  $< 10\text{ g}$  (BAM), (2) impact  $\sim 2\text{--}3\text{ cm}$  (type 12), and (3) spark  $< 0.25\text{ J}$ .<sup>43</sup>

## Results

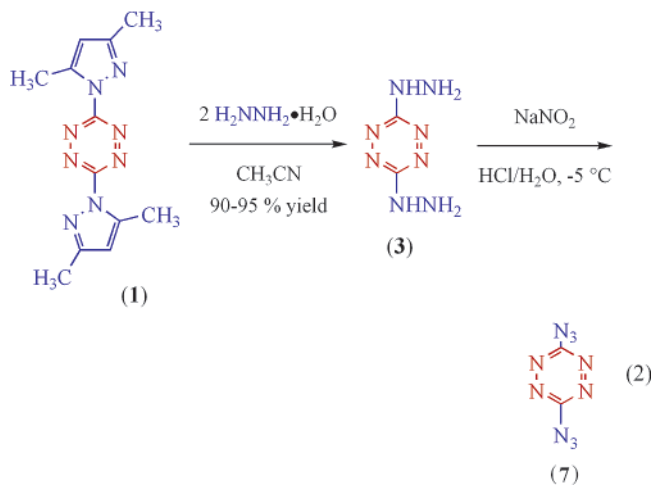
**Synthesis.** Monosubstituted azido 1,2,4,5-tetrazines have been previously reported in the literature.<sup>11,23,37,44</sup> In 1963, Marcus reported the preparation of **7** in which **5** underwent a nucleophilic substitution reaction to form **3** followed by diazotization by  $\text{NaNO}_2$ , eq 1.<sup>37</sup>



This reaction pathway was rather inefficient and costly because the reaction yield was low, and the expensive anhydrous

hydrazine was used as the solvent. Furthermore, no details on the physical as well as chemical characteristics and energetic properties of **7** were provided other than just a melting point of  $130^{\circ}\text{C}$ .

In our improved synthetic pathway shown in eq 2, bright magenta **1** rapidly reacted with 2 equiv of hydrazine hydrate in  $\text{CH}_3\text{CN}$  to give deep red **3** which underwent diazotization by  $\text{NaNO}_2$  to give **7**. The bright orange solid precipitated which was filtered, washed with fresh cold water, air-dried, and recrystallized using either  $\text{CH}_2\text{Cl}_2$  or  $\text{CHCl}_3$ .



Reminiscent of the preparation of **7**, the preparation of **6** is summarized in eq 3. A rapid reaction between **1** and 1 equiv of hydrazine hydrate in  $\text{CH}_3\text{CN}$  to form red **2** which was diazotized to give deep red **6**.

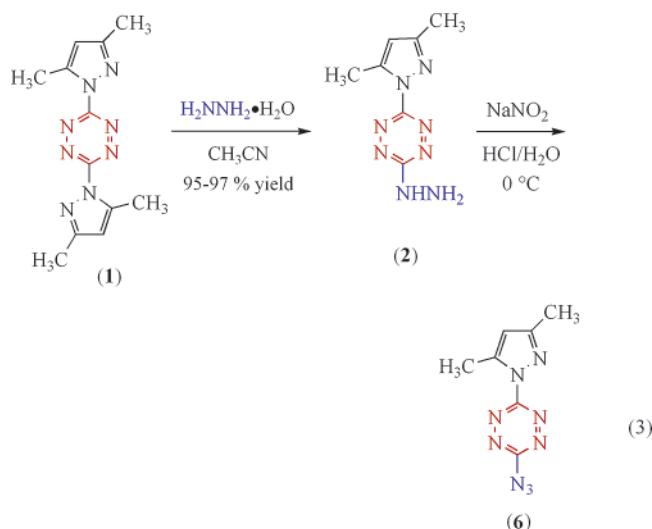
In our reaction pathways, the inexpensive hydrazine monohydrate was used in the preparations of **2** and **3**, and they both gave nearly quantitative yields.

**Infrared Spectroscopy and Heat of Formation ( $\Delta H_f$ ).** The infrared spectra of compounds **6** and **7** were obtained in Nujol mulls. In these spectra, significant differences between the two compounds appear in the region  $2100\text{--}2300\text{ cm}^{-1}$ . For **7**, two bands assigned to  $\nu_{\text{asym}}(\text{N}_3)$  are at 2169 and  $2207\text{ cm}^{-1}$ . The  $\nu_{\text{asym}}(\text{N}_3)$  for **6** appears at lower energy,  $2152\text{ cm}^{-1}$ . The experimental  $\Delta H_f$  values are  $+615\text{ kJ/mol}$  for **1**,  $+465\text{ kJ/mol}$  for **4**,  $+307\text{ kJ/mol}$  for **5**, and  $+858\text{ kJ/mol}$  for **6**.

**UV–Visible Spectroscopy.** UV–visible spectra for **1**, **6**, and **7** in chloroform are shown in Figure 1.

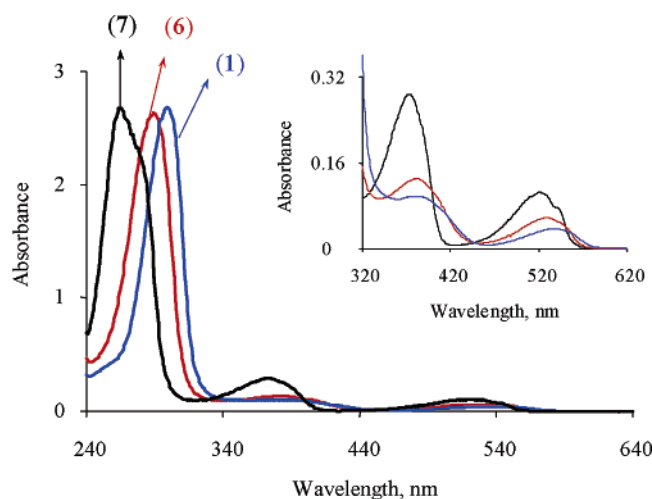
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**Redox Chemistry.** All cyclic voltammograms of tetrazine compounds provide evidence for chemically reversible couples on the cyclic voltammetric time scale at a scan rate from 200 to 800 mV/s at room temperature and at 80 °C. The redox potentials are  $-0.617$  V for **1**,  $-0.145$  V for **6**,  $-0.534$  V for **6A**,  $+0.518$  V for **7**, and  $-0.106$  V for **7A**. The redox potential of  $-0.472$  V for **7B** was collected at 80 °C.

**$^{13}\text{C}$  NMR Spectroscopy.** The resonances of **6**, **6A**, **7**, **7A**, and **7B** are strongly dependent upon the polarity of solvents used. In nonpolar solvents such as  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$ , the azido substituents retain their own identity. In polar solvents such as  $\text{CD}_3\text{CN}$ ,  $(\text{CD}_3)_2\text{CO}$ , and  $\text{CD}_3\text{OD}$ , **6** is converted to **6A**, whereas **7** undergoes azido-tetrazolo equilibrium. In a more polar solvent such as  $\text{DMSO}-d_6$ , **7** irreversibly transforms into the tetrazolo isomer. Selected resonances of the tetrazine parent ring are 158.98 ppm for **1** in  $\text{CDCl}_3$ , 164.46 and 159.34 ppm for **6** in  $\text{CDCl}_3$ , 152.12 and 150.35 ppm for **6A** in  $\text{DMSO}-d_6$ , 164.19 ppm for **7** in  $\text{CDCl}_3$ , 157.94 and 150.41 ppm for **7A** in  $\text{DMSO}-d_6$ , and 144.89 ppm for **7B** in  $\text{DMSO}-d_6$ . The  $^{13}\text{C}$  NMR data



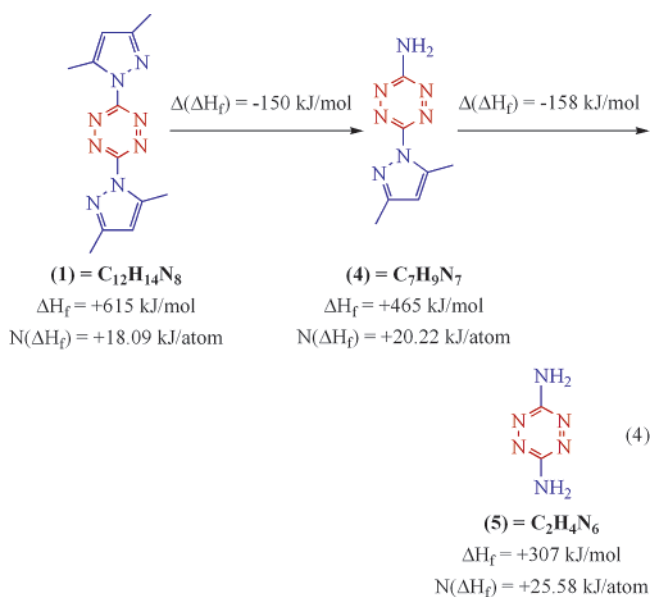
**Figure 1.** Absorption spectra in  $\text{CHCl}_3$ : Black = **7**, red = **6**, and blue = **1**. The spectral features are summarized in Table 1. The  $\pi \rightarrow \pi^*$  (tetrazine) band appears in the UV region at 265 nm for **7**, at 289 nm for **6**, and at 299 nm for **1**. Two additional transitions appear in the visible region at 373 and 521 nm for **7**, at 383 and 530 nm for **6**, and at 383 and 536 nm for **1**. In both UV and visible regions, all transitions shift to higher energy in the order of  $7 > 6 > 1$ .

for all compounds were obtained at room temperature, while the data for **7B** were collected at 80 °C.

## Discussion

**Heats of Formation.** The azido group is one of the most energetic functional groups known and has previously been reported to add 293 kJ/mol to the energy content of a molecule.<sup>45</sup> In addition, the tetrazine ring system contains a large inherent positive  $\Delta H_f$ .<sup>3</sup> Predictably, the combination of doubly substituted covalent azides with the tetrazine ring will lead to a molecule with a very large  $\Delta H_f$ . However, an experimental  $\Delta H_f$  for **7** cannot be measured because it is extremely sensitive to spark, friction, and impact.

To derive a reasonable  $\Delta H_f$  value for **7**, we proposed to use an additive method which appears to be valid by the  $\Delta H_f$  values of **1**, **4**, and **5**, eq 4.



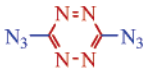

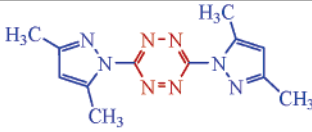
In this stepwise amino substitution, the  $\Delta H_f$  values for **1**, **4**, and **5** were experimentally measured as +615, +465, and +307 kJ/mol, respectively. Their normalized heats of formation ( $N\Delta H_f$ ) are correspondingly calculated as +18.09 kJ/atom for **1**, +20.22 kJ/atom for **4**, and +25.58 kJ/atom for **5**. As seen in eq 4, the first substitution of DMP by  $\text{NH}_2$  decreases  $\Delta H_f$  by 150 kJ/mol and increases  $N\Delta H_f$  by 2.13 kJ/atom. The second substitution further reduces  $\Delta H_f$  by 158 kJ/mol and raises  $N\Delta H_f$  by 5.36 kJ/atom. These data confirm that  $\Delta H_f$  of a symmetrically disubstituted tetrazine can be predicted if the heat of reaction of the first substituted step is known.

Extending this logic to **7**, we measured the  $\Delta H_f$  value for **6** from which the  $\Delta H_f$  value for **7** is derived accordingly. It is predicted to be +1101 kJ/mol. As shown in eq 5, the  $N\Delta H_f$  value for **7** is +91.75 kJ/atom which is the highest positive  $N\Delta H_f$  reported for all known organic molecule. Notably, the replacement by the first  $\text{N}_3$  increases  $N\Delta H_f$  by 19.21 kJ/atom, while the second  $\text{N}_3$  increases  $N\Delta H_f$  by an additional 54.45 kJ/atom. Compared to the stepwise amino-substituted data for

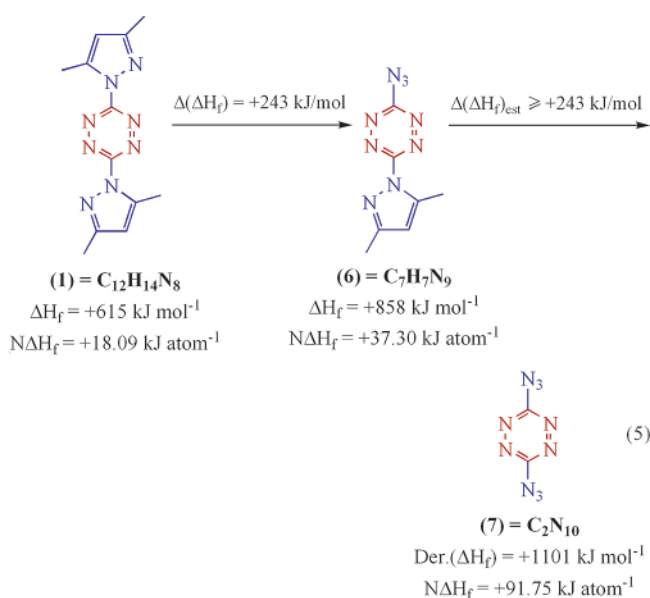
(45) Haiges, R.; Boatz, J. A.; Vij, A.; Gerken, M.; Schneider, S.; Schroer, T.; Christe, K. O. *Angew. Chem., Int. Ed.* **2003**, *42*, 5847–5851.



**Table 1.** UV–Visible Spectroscopy for Compounds **1**, **6**, and **7**

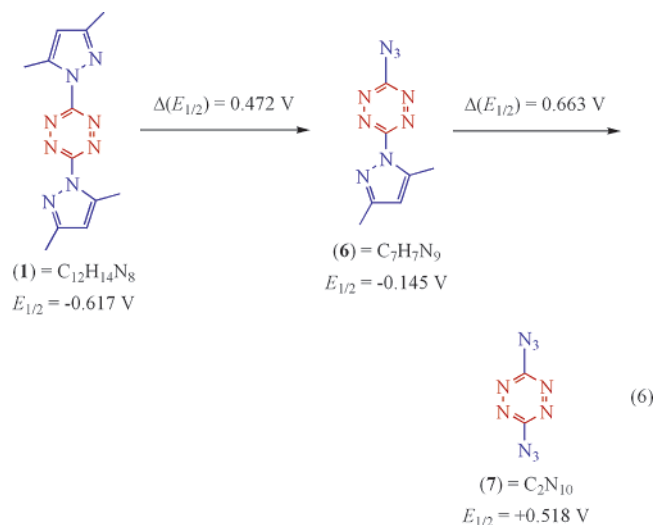
Compounds			
Wavelength, nm	265	289	299
$\epsilon(\text{M}^{-1} \text{cm}^{-1})$	$1.94 \times 10^4$	$1.91 \times 10^4$	$1.94 \times 10^4$
Wavelength, nm	373	382	383
$\epsilon(\text{M}^{-1} \text{cm}^{-1})$	$1.79 \times 10^3$	$8.14 \times 10^2$	$6.09 \times 10^2$
Wavelength, nm	521	530	536
$\epsilon(\text{M}^{-1} \text{cm}^{-1})$	$6.50 \times 10^2$	$3.58 \times 10^2$	$2.35 \times 10^2$

**5**, the energetic azido substituents dramatically enhance the energy content of **7**.

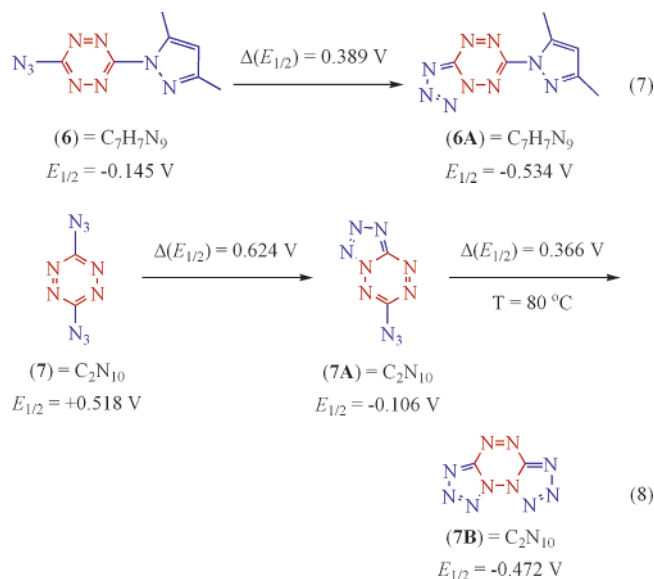


**UV–Visible Spectroscopy and Redox Chemistry.** As shown in Figure 1 and Table 1, the transition in the UV region shifts from low energy in **1** to high energy in **6** and to higher energy in **7**; however, their extinction coefficients essentially remain the same. In the visible region, the transition energies increase proportionally with their extinction coefficients. The higher energy of the transition bands of **6** compared to those of **1** are consistent with the decrease in  $E_{1/2}$  from  $-0.145 \text{ V}$  for **6** to  $-0.617 \text{ V}$  for **1** ( $\Delta E_{1/2} = 0.472 \text{ V}$ ). Similarly, the transition bands for **6** appear at lower energy than those for **7** which is also consistent with the decrease in  $E_{1/2}$  from  $+0.518 \text{ V}$  for **7** to  $-0.145 \text{ V}$  for **6** ( $\Delta E_{1/2} = 0.663 \text{ V}$ ), eq 6.

The cyclic voltammetric data also reveal that the  $E_{1/2}$  values are dependent on the substituent and its conformation. The first replacement of DMP in **1** by  $\text{N}_3$  in **6** increases the  $E_{1/2}$  value by 472 mV, while the second replacement of DMP in **6** by  $\text{N}_3$  in **7** raises the  $E_{1/2}$  value by 663 mV. The higher  $\Delta E_{1/2}$  value of the second step compared to the  $\Delta E_{1/2}$  value of the first step ( $663 \text{ mV} > 472 \text{ mV}$ ) illustrates that the first  $\text{N}_3$  substitution is easier than the second  $\text{N}_3$  substitution, which is consistent with the synthetic results.

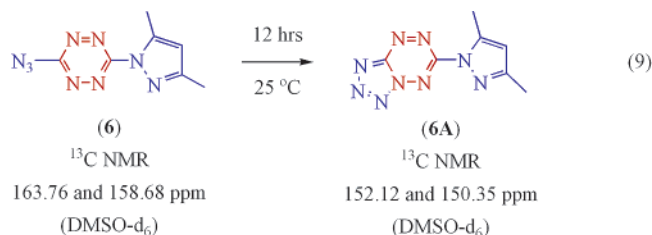


The smaller  $\Delta E_{1/2}$  of 389 mV in eq 7 compared to  $\Delta E_{1/2}$  of 624 mV in eq 8 reveals that the azido-tetrazolo transformation from **6** to **6A** is electronically more favorable than that from **7** to **7A**. With a required additional potential energy of 366 mV, the conversion from **7** to **7B** is expectedly more difficult. This uphill process only occurs in DMSO at temperature of at least  $80^\circ \text{C}$ .

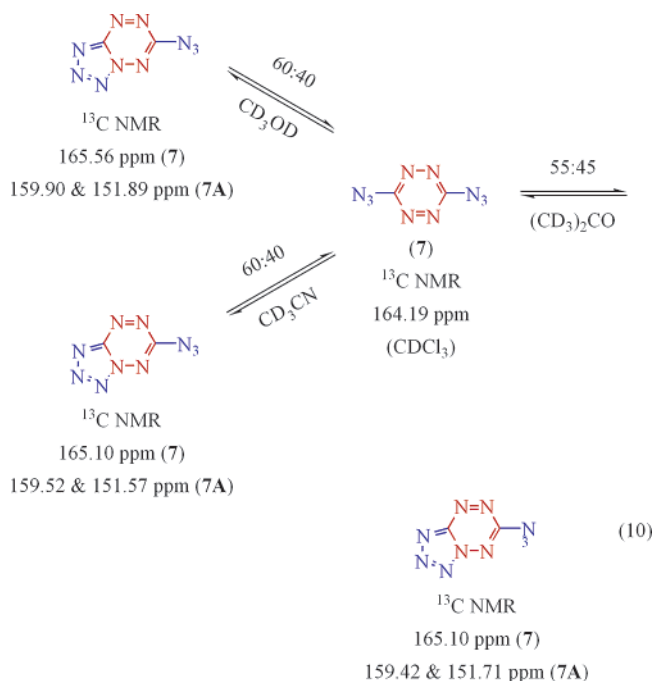


**$^{13}\text{C}$  NMR.** The azido-tetrazolo tautomerization and tetrazolo transformation were further investigated in details by the  $^{13}\text{C}$  NMR study. The conversions are strongly dependent on the solvent polarity and the nature of the second substituent on the tetrazine ring as well as its conformation. For example, the conversion from azido **6** to tetrazolo **6A** occurred favorably at room temperature in polar solvents. A similar phenomenon was also observed for 3-amino-6-azido-1,2,4,5-tetrazine.<sup>23</sup>

Compound **6** displayed two  $^{13}\text{C}$  signals at 164.46 and 159.34 ppm for the tetrazine parent ring in  $\text{CDCl}_3$ . As shown in eq 9, the two resonances that initially appeared at 163.76 and 158.68 ppm were shifted to 152.12 and 150.35 ppm after a 12-h period at room temperature in  $\text{DMSO}-d_6$ .



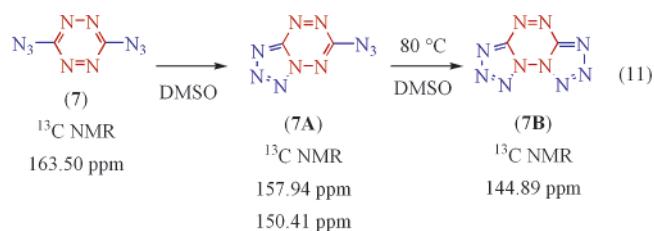
When the second DMP group was replaced by the azido substituent to form **7**, a single resonance at 164.19 ppm was observed in  $\text{CDCl}_3$ . In the more polar solvents, the ratios of the azido:tetrazolo equilibrium were 55:45 for  $(\text{CD}_3)_2\text{CO}$  and 60:40 for  $\text{CD}_3\text{OD}$  and  $\text{CD}_3\text{CN}$ , eq 10.



In  $\text{DMSO}-d_6$ , a single signal at 163.50 ppm rapidly diminishes, while two signals at 157.94 and 150.41 ppm appear with the same rate at room temperature. At 80  $^\circ\text{C}$ , only one signal at 144.89 ppm is observed, eq 11.

The downfield shifts from 163.5 ppm for **7** to 157.94 and 150.41 ppm for **7A** and to 144.89 ppm for **7B** are consistent with the decrease in redox potentials from **7** to **7A** and to **7B**.

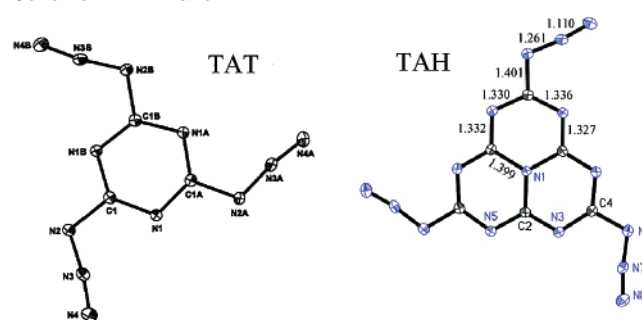
The cyclic voltammetric data in eqs 7 and 8 confirm that the conversions **6**  $\rightarrow$  **6A**, **7**  $\rightarrow$  **7A**, **7A**  $\rightarrow$  **7B**, and **7**  $\rightarrow$  **7B** are all electronically favorable; however, the experimental data reveal



that the transformation **7A**  $\rightarrow$  **7B** has a substantial activation energy barrier. As mentioned previously, the transformation from **7A** to **7B** only occurs when the temperature is at least at 80  $^\circ\text{C}$ .

**Comparisons to Other Polyazido Heteroaromatic Triazine-Based Compounds.** 2,4,6-Tri(azido)-1,3,5-triazine (TAT) is known to remain as triazido triazine in solutions and in the solid state as confirmed by X-ray crystallography, Scheme 4.<sup>46</sup>

**Scheme 4.** TAT and TAH



TAT is readily soluble in most common solvents such as benzene, chloroform, ether, alcohols, acetone, DMF, and DMSO, but it does not undergo azido-tetrazolo tautomerization. Crystalline material melts at 94  $^\circ\text{C}$  (2  $^\circ\text{C}/\text{min}$ ) and slowly decomposes when the temperature reaches 180  $^\circ\text{C}$ .

Of the triazidotriazine-based family, 2,5,8-tri(azido)-s-heptazine (TAH) is another member that possesses properties similar to those of TAT. On the NMR time scale, there was also no evidence of azido-tetrazolo tautomerization in most solvents including DMSO.<sup>16</sup> In both molecular structures shown in Scheme 4, the three azido groups of TAT and TAH are oriented in a  $\text{C}_3$ -propeller shape revolving around the triazine-based frameworks.

4,4',6,6'-tetra(azido)hydrazo-1,3,5-triazine (TAHT) and two polymorphs (one of which has two conformers) of 4,4',6,6'-tetra(azido)azo-1,3,5-triazine (TAAT) are polyazido substituted triazine-based compounds.<sup>5,8</sup> Although four azido substituents in each molecule linearly arrange themselves in combinations of different orientations, no evidence of either azido-tetrazolo tautomerization or transformation has been observed, Scheme 5.<sup>5,8</sup>

As a consequence, the absence of azido-tetrazolo tautomerization in these triazine-based compounds clearly reveals that orientation and steric effect of azido substituents are not the factors influencing the ring closure.

Unlike polyazido substituted triazine-based materials, **7** undergoes azido-tetrazolo equilibria in  $(\text{CD}_3)_2\text{CO}$ ,  $\text{CD}_3\text{CN}$ , and  $\text{CD}_3\text{OD}$  and transforms to tetrazolo isomer in  $\text{DMSO}-d_6$ . Given the propeller orientation of two azido substituents in Scheme

(46) Kessenich, E.; Klapotke, T. M.; Knizek, J.; Noth, H.; Schulz, A. *Eur. J. Inorg. Chem.* **1998**, 12, 2013–2016.

