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Photolysis of bis(1*H*-tetrazol-5-yl)amine (H_2BTA), a high nitrogen content tetrazole-based energetic compound in water

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ABSTRACT

Tetrazoles have wide industrial applications, notably in the pharmaceutical industry. Tetrazole derivatives, such as bis(1*H*-tetrazol-5-yl)amine (H_2BTA) with a nitrogen content of 82.34%, have recently been considered by the defense industry as high nitrogen composite propellants. Little information is available on their environmental fate. Photodegradation studies under solar simulating conditions showed that H_2BTA was partially degraded in water, while it was completely degraded under UV light at $\lambda = 254$ nm. When H_2BTA (0.35 mM) was irradiated with simulated sunlight at pH 3.65, there was a 1-day lag phase before the chemical started to degrade, reaching 43.5% degradation after 7 days. However, when pH increased to 5.76, H_2BTA degraded without lag phase, suggesting that an $HBTA^-$ anion was involved in the initial degradation of the chemical. 5-Aminotetrazole (5-AT) was identified as a final degradation product and *N*-(1*H*-tetrazol-5-yl)formamide (T(5yl)FA) and 1*H*-tetrazol-5-ylcarbamic acid (T(5yl)CA) as intermediate products. At $\lambda = 254$ nm, H_2BTA (0.35 mM, pH 3.65) disappeared rapidly, resulting in the loss of 94% after 65 min. 5-AT was detected together with several transient products including *N*-(1*H*-tetrazol-5-yl)carbamohydrazonic acid (T(5yl)CHA) and T(5yl)FA. Kinetic studies and products analysis revealed that H_2BTA photodegraded via two initial routes. One route (*a*) marked by the initial loss of HN_3 and another (*b*) marked by the initial loss of N_2. Route *a*) was characteristics for irradiation with simulated sunlight; however, routes *a*) and *b*) proceeded simultaneously under UV light. 5-AT eventually degraded to presumably give N_2 and/or HN_3 using UV light. Understanding the photodegradation pathway of H_2BTA under simulated sunlight can help in providing the basis for natural attenuation assessment of the chemical in contaminated aquatic environments.

Keywords: H_2BTA; photodegradation; energetic chemical; environmental fate

1. Introduction

Tetrazoles are five-membered heterocyclic compounds having one carbon and four nitrogen atoms arranged in planar rings. Tetrazole derivatives have wide applications in major industrial areas such as medicinal chemistry, coordination chemistry, agricultural technology, imaging technology, and in the automobile industry as gas generators for airbags (Frija et al., 2010). Recently, they have been considered by the defense industry as high nitrogen composite propellants (Klapötke et al., 2008; Yuan and Bernstein, 2016; Lavoie et al., 2017). For example, in order to design a low erosivity gun propellant, emphasis should be put on lowering the flame temperature and increasing nitrogen content in the combustion gases. The nitrogen-rich (N% = 82.34%) bis(1*H*-tetrazol-5-yl)amine (H_2BTA), an amine substituted with two tetrazole rings, fits perfectly under that role. It goes without saying that new propellants designed to have lower erosivity should also provide equal or better performance than the propellants they are designed to replace. The positive effects of nitrogen-rich materials such as H_2BTA on the burning rate of propellants and also on the gun barrel-like steel erosion have already been demonstrated by Lavoie et al. (2017, 2018). These results point toward the H_2BTA becoming a very suitable candidate for the future gun propellants. Although tetrazole derivatives are extensively studied, H_2BTA is poorly characterized from the environmental chemistry perspective.

Some data on synthesis, structural attributes and isomeric distribution of the amine derivatives of tetrazoles are useful to help understand the environmental chemistry and fate of H_2BTA. The most common way to form tetrazoles is cycloaddition between an organic nitrile (R-CN) and an organic azide ($R\text{-}N_3$) or azide salts. The acid-catalyzed cyclization reaction of sodium dicyanamide and sodium azide in a ratio of 1:2 generates H_2BTA (Klapötke et al., 2008). The hydrogen atom bound to the N-ring of tetrazole is labile and, depending on the chemical environment, the molecules can be deprotonated or protonated to form the corresponding anions or cations, respectively (Friedrich et al., 2005; Guo et al., 2010; Li et al., 2015; Liu et al., 2017) (Fig. 1, top), or interconverted into different tautomers called prototropic tautomers (Paul et al., 2009; Nelson and Baglin, 1972) (Fig. 1, middle). The predominant tautomeric forms of tetrazoles substituted on the carbon atom (5-substituted) are mainly the 1*H*-form in the solid state and 2*H*-forms in the gas phase. In nonpolar solvent, the tautomeric preference of tetrazole with an electron releasing substituent (e.g. 5-aminotetrazole, 5-AT) is the same as in the gas phase, i.e., the 2*H*-form, while in a solvent with high dielectric constant, like water, the 1*H*-form is dominant (Najafi Chermahini et al., 2007a). The cyclic tetrazoles can also reversibly convert to an acyclic azide where both forms can exist in equilibrium with each other (Fig. 1, bottom).

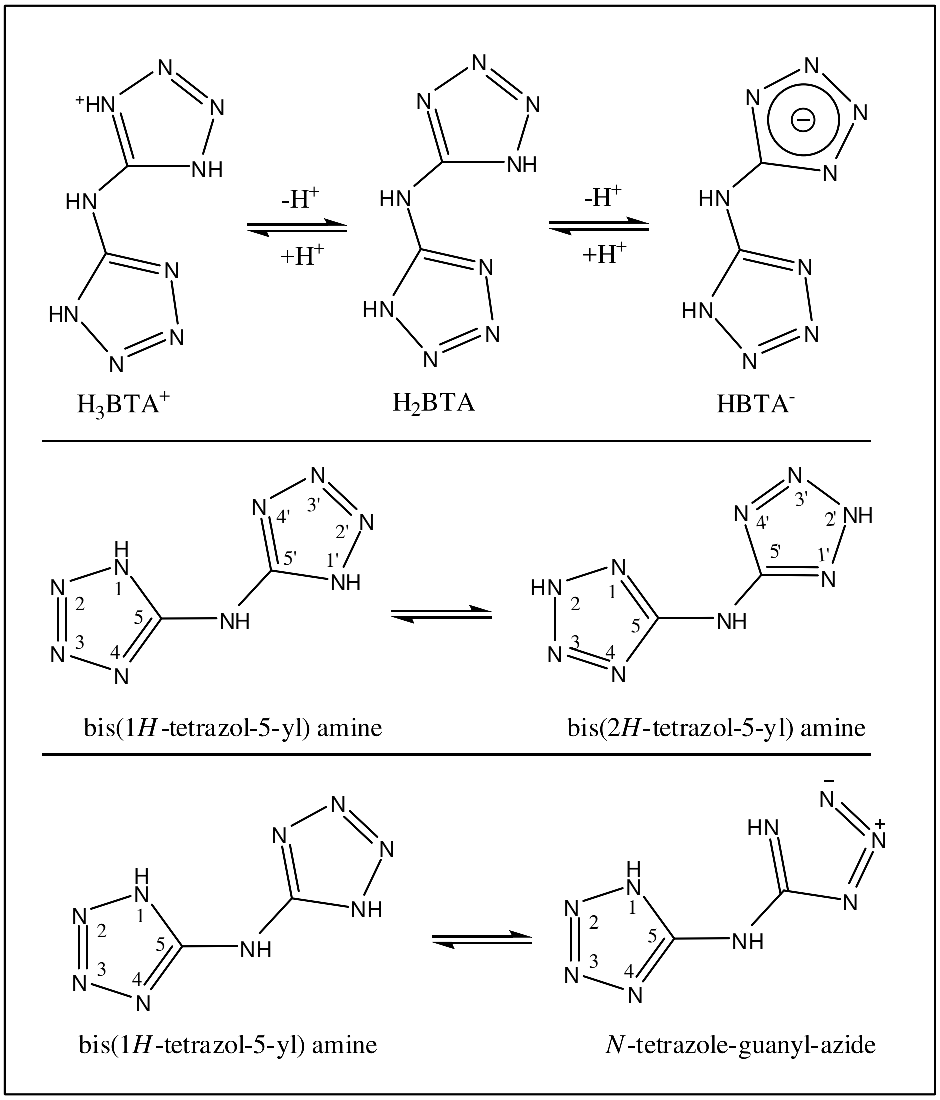


Fig. 1. Chemical structures of H_2BTA (bis(1*H*-tetrazol-5-yl)amine) and its protonated H_3BTA^+ and deprotonated $HBTA^-$ ions (top); bis(1*H*-tetrazol-5-yl)amine and its prototropic tautomer bis(2*H*-tetrazol-5-yl)amine (middle); and azido isomer (*N*-tetrazole-guanyl-azide) (bottom).

Tetrazole and its 5-substituted derivatives are weak acids with p*K*a values in the range of 1.1−6.3, which is comparable to carboxylic acids (e.g. CH_3COOH, p*K*a = 4.75). The tetrazolic acid fragment $–CN_4H$ has acidity similar to the carboxylic acid group, $–CO_2H$, but is metabolically more stable at physiological pH 7.4 (Frija et al., 2010). The reported p*K*a value for tetrazole is 4.70, and two values were measured for 5-AT, 1.76 (pKa$_1$) and 5.95 (pKa$_2$) (Boraei, 2001). Two p*K*a values of 1.41 (pKa$_1$) and 4.25 (pKa$_2$) have also been reported for 5,5'-bitetrazole, a compound containing two tetrazole rings (Trifonov and Ostrovskii, 2006). H_2BTA can be deprotonated reversibly to form mainly mono- and bi- and occasionally trivalent anions. The p*K*a values of H_2BTA have not yet been reported. The anions of H_2BTA easily form salts with metals or nitrogen-rich bases such as ammonium, hydrazinium and guanidium derivatives (Guo et al., 2010; Li et al., 2015; Liu et al., 2008).

Photochemistry of mono- or bi-substituted tetrazoles (e.g. 5-methyltetrazole, 5-phenyltetrazole and 2-methyl-2*H*-tetrazol-5-amine) have been widely studied, whereas photodegradation of H_2BTA, the intended energetic chemical in the present study, is poorly investigated. Reportedly tetrazole can undergo various photodegradation pathways depending on the nature of the substitution(s) on the ring. For example, Maier and coworkers (1996) reported rapid cleavage of the unsubstituted tetrazole ring during photolysis, leading to the extrusion of two nitrogen atoms and the formation of several photoproducts, including nitrilimine, nitrene/hydrogen cyanide (HN···HCN) complex, diazomethane, carbodiimide and cyanamide. Nitrogen releases have also been reported during photolysis of mono-substituted tetrazoles such as 5-phenyltetrazole in THF at λ=254 nm and 5-methyltetrazole in solid argon using tunable UV laser radiation. In addition, 1,2-dihydro-3,6-diphenyl-1,2,4,5-tetrazine from 5-phenyltetrazole (Scheiner and Dinda Jr., 1970) and *C*-methylnitrilimine, *N*-methylcarbodiimide and methylcyanamide from 5-methyltetrazole (Pagacz-Kostrzewa et al., 2014) have been identified as main degradation products. During UV irradiation ($\lambda > 235$ nm) of di-substituted 2-methyl-2*H*-tetrazol-5-amine in solid argon, several degradation pathways were identified including 1) elimination of N_2 with the production of 1-methyl-1*H*-diazirene-3-amine, 2) cleavage of the tetrazole ring leading to the production of methylazide and cyanamide, and 3) tautomerization of the tetrazole to mesoionic 3-methyl-1*H*-tetrazol-3-ium-5-aminide (Gomez-Zavaglia et al., 2005). The primary formation of N_2 and HN_3 has also been observed during thermal degradation of 5-aminotetrazole (Brill and Ramanathan, 2000; Kiselev and Gritsan, 2009; Paul et al., 2009; Piekiel and Zachariah, 2012). The photolysis of H_2BTA by two photon laser excitation led to the initial cleavage of the N1-N2 bond (for numbering see Fig. 1, middle) followed by the formation of N_2 (Yuan and Bernstein, 2016). No other details were reported on the degradation products and other secondary degradation routes.

The aim of this work was to provide data on the photodegradation of H_2BTA in water using simulated sunlight and ultraviolet light.

2. Materials and methods

2.1. Chemicals

N,N-bis(1*H*-tetrazol-5-yl)amine monohydrate, $H_2BTA{\cdot}H_2O$, was synthesized by Defense Research and Development Canada (DRDC)-Valcartier according to the procedures previously described by Klapötke et al. (2008). The purity of the material was verified through hydrogen, carbon and nitrogen nuclear magnetic resonance spectroscopy. 5-Aminotetrazole monohydrate was purchased from Sigma-Aldrich (Canada). Working solutions of H_2BTA (0.35 mM or 0.18 mM) and 5-AT (0.2 mM) were prepared in deionised water. The pH of the H_2BTA (0.35 mM) solution was 3.65; in some assays, the pH of the solution was adjusted to 5.76 and 8.05 with NaOH (0.5% w/v) prior to photolysis.

2.2. Irradiation experiments

Irradiation experiments were conducted using artificial sunlight generated from a SolSim solar simulating photoreactor (Luzchem Research Inc., Canada). The total power of the solar simulator output spectrum was calibrated to the best approximation of ASTM Air Mass 1.5 Global Tilt Standard in the 280-800 nm regions: total irradiance of 590,000 mW m^{-2}. To accelerate the degradation process, a Rayonet photoreactor (Branford, CT) equipped with 16 ultraviolet lamps (wavelength 254 nm) was also used. In a typical experiment, 5 mL of aqueous solutions of H_2BTA (0.35 mM or 0.18 mM) or 5-AT (0.2 mM) in 20 mL quartz tubes were irradiated in either SolSim or Rayonet photoreactors at room temperature. The experiments were carried out in duplicates or triplicates.

2.3. Analytical methods

H_2BTA and 5-AT were quantified by a Waters HPLC system (Milford, MA, USA) equipped with a model 2996 photodiode array detector, a model 600 pump, a model 717 plus injector, and a temperature control module. Aliquots (10 µL) were injected on a Gemini-NX-C18 column (150 x 4.6 mm, 3 µm) (Phenomenex, Torrance, CA) at 40°C. The mobile phase (0.1% phosphoric acid (pH 2.2) and methanol, 90%:10%) was run isocratically at 0.5 mL min^{-1}. Quantification was performed at a wavelength of 230 nm. The instrumental detection limit was estimated to be 0.01 mg L^{-1} for both chemicals.

The degradation products were analyzed by liquid chromatography–mass spectrometry (LC-MS) using a MicrOTOF-Q mass analyzer (Bruker) attached to an HPLC system (Agilent 1200 Series) equipped with a DAD detector. Aliquots (10 μL) were injected into a 3 micron-pore size Luna Phenyl-Hexyl column (2 μm ID × 150 mm; Phenomenex, USA) at 25°C. The solvent system was composed of a mixture of MeOH and 0.05% v/v HCOOH in water (10%:90%) at a flow rate of 0.15 mL min^{-1}. For mass analysis, negative electrospray ionization mode (ESI-) was used producing mainly deprotonated molecular mass ions [M-H]$^-$. The mass range was selected from 40 to 1000 *m/z*. The pH measurements were carried out with a Mettler Toledo pH meter.

3. Results and discussion

3.1. Irradiation of H_2BTA by simulated sunlight

When H_2BTA (0.35 mM, pH 3.65) was irradiated in a solar simulator (SolSim), only a minute amount of the chemical disappeared after 1 day, then the H_2BTA concentration decreased linearly with time (Fig. 2). A loss of 43.5% was measured after 7 day. Photodegradation started immediately but very slowly for the first 2 days at the lower concentration (0.18 mM, pH 3.98), reaching only 28% of degradation after 8 days of irradiation (Fig. 2).

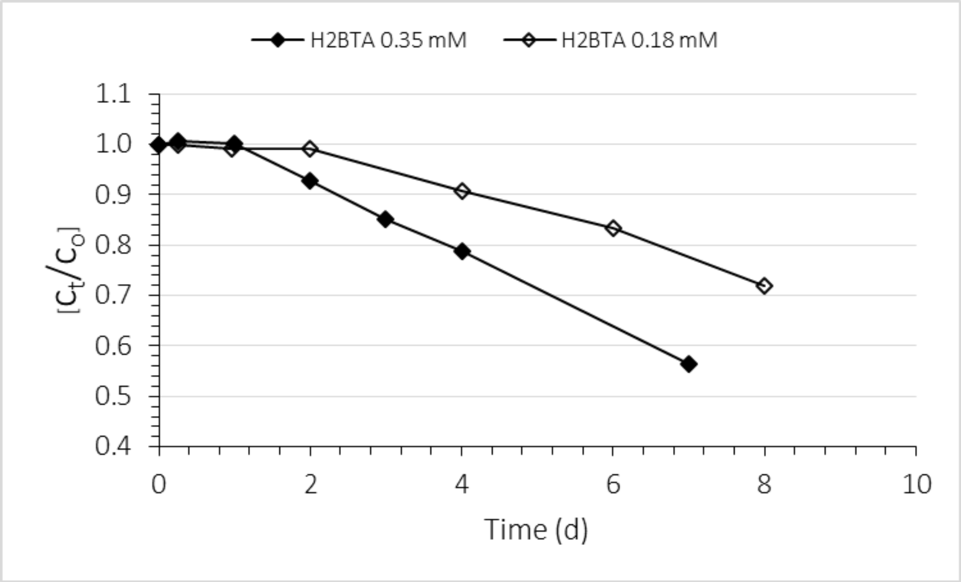


Fig. 2. H_2BTA photodegradation under simulated sunlight. The disappearance of the starting material showed a RSD of less than 5%.

HPLC/UV analysis of the H_2BTA solution (0.35 mM) irradiated in the SolSim reactor showed a peak at 4.0 min that was identified as 5-AT by comparison with a commercially available reference standard (Fig. 3). Two other peaks were observed at 4.55 and 4.76 min (Fig. 3). LC-MS ESI- analysis of the compound eluted at 4.55 min showed an $[M-H]^-$ molecular mass ion of *m/z* 128.026 and was tentatively identified as 1*H*-tetrazol-5-ylcarbamic acid, T(5yl)CA (chemical formula: $C_2H_3N_5O_2$, exact molecular mass: 129.029). In the same way, the compound eluted at 4.76 min showing a $[M-H]^-$ molecular mass ion *m/z* 112.030 was tentatively identified as *N*-(1*H*-tetrazol-5-yl)formamide, T(5yl)FA (chemical formula: $C_2H_3N_5O$, exact molecular mass: 113.034).

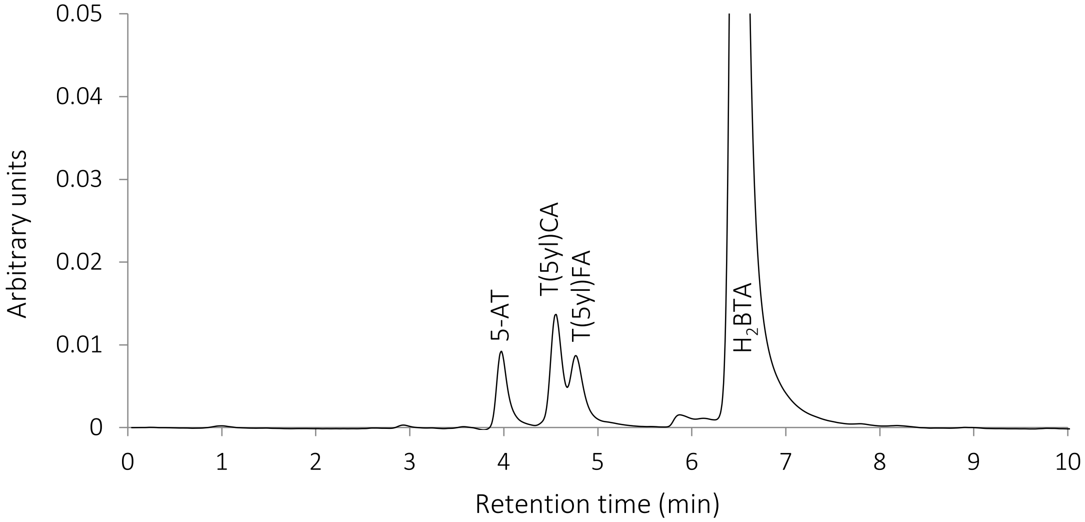


Fig. 3. HPLC/UV chromatogram of H_2BTA (0.35 mM, pH 3.65) photolyzed in a solar simulator for 7 days.

While trace amounts of T(5yl)FA and T(5yl)CA were detected after 1 day, formation of 5-AT did not begin until day 2 (Fig. S1), suggesting that T(5yl)FA (*N*-(1*H*-tetrazol-5-yl)formamide) and T(5yl)CA (1*H*-tetrazol-5-ylcarbamic acid) could be the precursors of 5-AT. The highest yields of 5-AT, 0.43 and 0.39 moles for each mole of H_2BTA degraded (using 0.35 mM and 0.18 mM, respectively), were measured after 2 days of irradiation and then decreased to 0.26 moles in both cases after 7 and 8 days of photolysis in SolSim, respectively. Due to the demonstration in a separate experiment of the very slow degradation of 5-AT (0.2 mM) by artificial sunlight (only 2.5% degraded after 8 days), we suspect that the transformation of one or more of the presumed precursors of 5-AT occurred at a slower rate than their formation.

The initial pH (3.65) of the 0.35 mM H_2BTA solution decreased to 3.50 after 4 days of irradiation in SolSim, suggesting slow deprotonation of H_2BTA to form $HBTA^-$ anions. Since p*K*a values of H_2BTA in water are unknown, it can only be estimated that at pH 3.65, H_2BTA is poorly dissociated in water, but its dissociation might increase by the influence of light energy. Interestingly, in the presence of a greater amount of $HBTA^-$ anions, e.g. at pH 5.76 adjusted with a small amount of NaOH (0.5%), photodegradation started immediately without a lag phase (Fig. S2), suggesting that $HBTA^-$ anions could be involved in the initial photodegradation of H_2BTA. However, at pH 8.0, H_2BTA did not degrade after 3 days of irradiation with simulated sunlight. We hypothesize that, at this pH, dissociation of H_2BTA is more pronounced, leading to the formation of the dianion BTA^{2-} with a higher aromaticity, and thus more stability, than the $HBTA^-$ anion.

3.2. Irradiation of H_2BTA by UV at λ=254 nm

H_2BTA in water (0.35 mM, pH 3.65 and 0.18 mM, pH 3.98) irradiated in a Rayonet photoreactor at λ=254 nm disappeared rapidly, resulting in a loss of 94% after 65 min and of 98% after 40 min, respectively (Fig. 4). The plot of $\{1/[c]_t\}$ vs time for the 0.35 mM experiment gave a straight line with slope k = 0.666 mM^{-1} min^{-1} (r^2 =0.999), indicating that photolysis of H_2BTA proceeded with second-order kinetics (Fig. S3). A half-life of 4.29 min was calculated. On the other hand, plotting $\{\ln[c]_t\}$ vs time for the 0.18 mM experiment gave a straight line with slope k = -0.1 min^{-1} (r^2 =0.995) indicating that photolysis of H_2BTA proceeded via a first-order kinetics (Fig. S4). A half-life of 6.92 min was calculated. Changing the order of a chemical reaction by changing the initial concentration of the reactant is an indication that the reaction proceeds via mixed-order kinetics, a characteristic of a complex (multi-step) reaction.

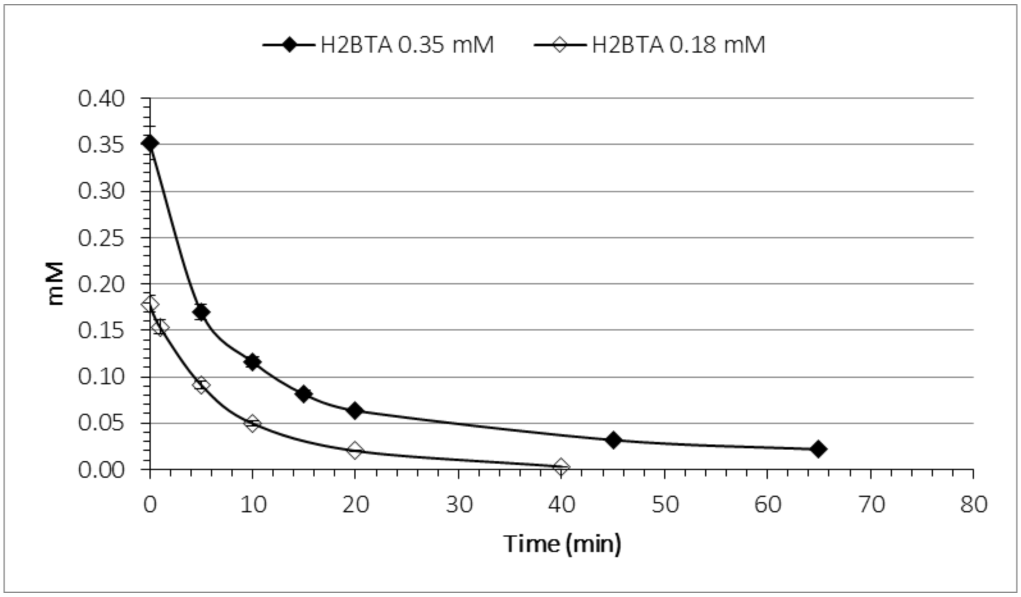


Fig. 4. Degradation of H_2BTA in water (0.35 mM, pH 3.65 and 0.18 mM, pH 3.98) during irradiation at $\lambda = 254$ nm. The disappearance of the starting material showed a RSD of less than 5%.

During degradation of H_2BTA (0.35 mM) with UV light, production of 5-AT was observed, but T(5yl)CA was not detected. T(5yl)FA appeared only in traces after 40 min of irradiation. Instead, HPLC/UV showed a new peak at 3.45 min (Fig. 5) that was tentatively identified by LC-MS as *N*-(1*H*-tetrazol-5-yl)carbamohydrazonic acid, T(5yl)CHA (chemical formula: $C_2H_5N_7O$, exact molecular mass: 143.055), a water adduct of nitrile imine derivative produced by the photochemical extrusion of N_2 from H_2BTA. The photoinduced rupture of the tetrazole ring ($\lambda < 290$ nm) and water addition to the 1,3-dipolar nitrile imine generated was reported by Herner and Lin (2016). Quenching of the nitrile imine intermediate by H_2O produced during photolysis of a peptide tetrazole at λ=302 nm was also described by Song et al. (2008).

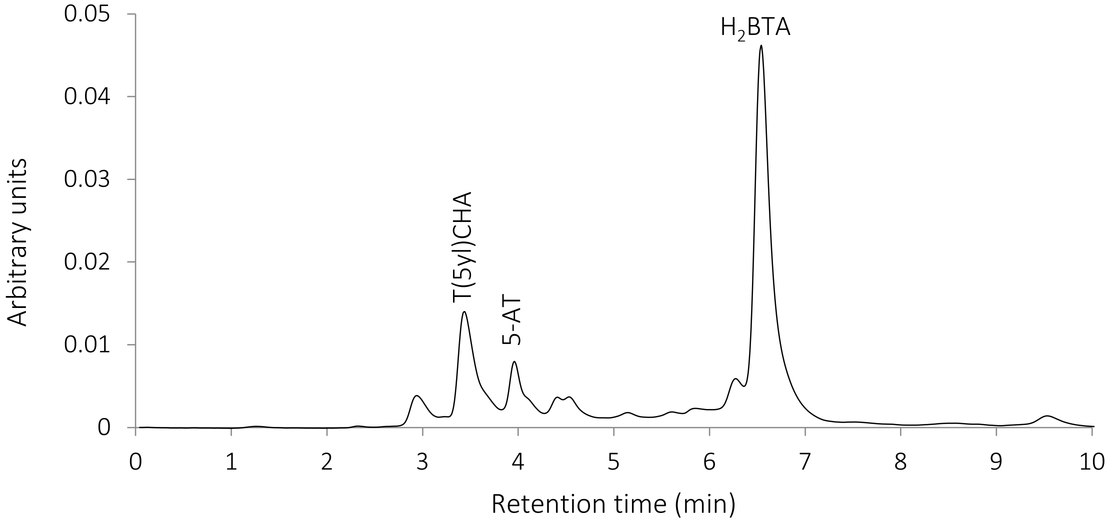


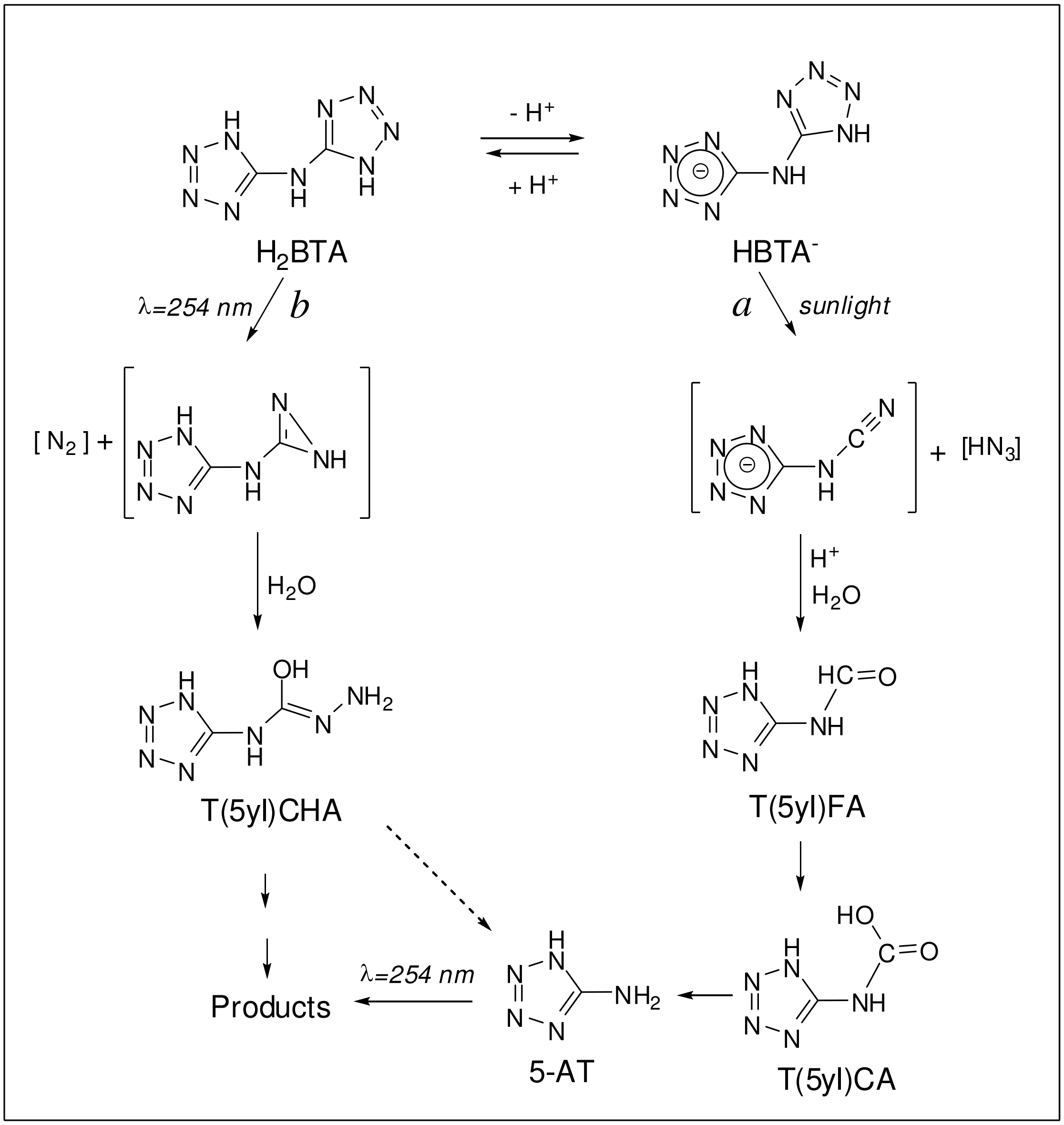
Fig. 5. HPLC/UV chromatogram of H_2BTA (0.35 mM, pH 3.65) photolyzed at λ = 254 nm for 20 min.

Formation of T(5yl)CHA peaked between 10 min and 20 min then slowly decreased; however, 5-AT remained almost constant (Fig. S5). The yields of 5-AT were only 0.06 and 0.09 moles for each mole of degraded H_2BTA, for initial concentrations of 0.35 and 0.18 mM, respectively, after 40 min of irradiation. When 5-AT (0.2 mM) was irradiated in a separate experiment, 91% of the compound was degraded after 40 min, slightly less than the degradation of H_2BTA (98% of 0.18 mM) under the same conditions, suggesting that 5-AT was produced and transformed with almost similar rates, which explains the low 5-AT yields observed during photolysis of H_2BTA at λ = 254 nm.

3.3. H_2BTA photodegradation pathways

The photodegradation of H_2BTA at pH 3.65 by simulated sunlight began with a relatively long lag phase (1 day). In addition, the pH decreased slightly, which can be explained by the deprotonation of H_2BTA, forming $HBTA^-$ anions. An increase in the initial degradation rate was observed at pH 5.76 when irradiated with simulated sunlight, suggesting that $HBTA^-$ anions are involved in the photodegradation of H_2BTA. Detection of the T(5yl)FA and T(5yl)CA intermediates and 5-AT indicates that only one tetrazole ring was cleaved during photolysis of H_2BTA by artificial sunlight (Scheme 1; pathway ***a***). We hypothesize that deprotonation of the ring-NH group might have modified the ring aromaticity thus facilitating isomerization, i.e., azido-tetrazole rearrangement, of the second tetrazole ring leading to the loss of HN_3. The loss of HN_3 from the anion forms of an 1*H*-tetrazol-5-yl derivative, N3,N6-bis(1*H*-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (Fig. S6), during ESI- mass spectrometry measurement has been reported previously (Parvari et al., 2018). The authors found that the activation energy for HN_3 loss is considerably lower than those of the proton-migration-dependant fragmentation leading to loss of N_2 (Parvari et al. 2018). When one of the two tetrazole rings of H_2BTA is destroyed, the 5-amino group can stabilise the second tetrazole ring (Cubero et al., 1998), resulting in greater resistance of 5-AT to photolysis with simulated sunlight.

Compound T(5yl)CHA was only detected in samples irradiated with UV light (λ = 254 nm), suggesting that a second pathway also occurred under this condition. H_2BTA can also be degraded by extruding N_2 from one of the two tetrazole rings producing the presumed nitrile imine-H_2O adduct T(5yl)CHA (Scheme 1; pathway ***b***). In situ formation of nitrile imine upon UV irradiation of tetrazoles derivatives and its reactivity with water has been reported (Song et al. 2008; Herner and Lin, 2017), but never observed during photolysis of the energetic chemical H_2BTA in water. T(5yl)CHA was unstable and degraded like 5-AT to unidentified products (Scheme 1; pathway ***b***).



Scheme 1. Postulated main degradation pathways during photolysis of H_2BTA in water; a) with simulated sunlight and b) with UV (λ=254 nm).

The possibility of transforming T(5yl)CHA into intermediate 5-AT cannot be ruled out; however, LC-MS detection of trace amounts of T(5yl)FA in samples irradiated for 40 min and 65 min suggests that both pathways *a* and *b* occurred simultaneously (Scheme 1) during UV irradiation.

Conclusion

The nitrogen-rich compound H_2BTA was partially degraded in water under solar simulating conditions and completely with UV light. The kinetic study and products analysis revealed that photo-transformation of H_2BTA with simulated sunlight was governed by a major pathway; however, a second degradation path appeared simultaneously during UV irradiation (λ = 254 nm). We proposed a photodegradation pathway triggered by two independent initial routes: a) one initiated by the loss of HN_3 and b) another initiated by the loss of N_2 to eventually give 5-AT. 5-AT remained relatively stable under simulated sunlight, but was degraded to unidentified products by UV light. Apart from the present study showing the potential photoremoval and thus natural attenuation of H_2BTA in contaminated water bodies, no other information is available on the fate and toxicity of H_2BTA in the environment. It is thus worth investigating whether 5-AT, a key degradation product of H_2BTA, is more or less toxic than the parent compound. As this chemical has a high probability of being used in future insensitive and high energy propellant formulations, the study of its environmental fate will contribute to a risk assessment prior to deployment in ranges and training areas.

Acknowledgment

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Supporting Information

Photolysis of bis(1*H*-tetrazol-5-yl)amine (H_2BTA), a high nitrogen content tetrazole-based energetic compound in water

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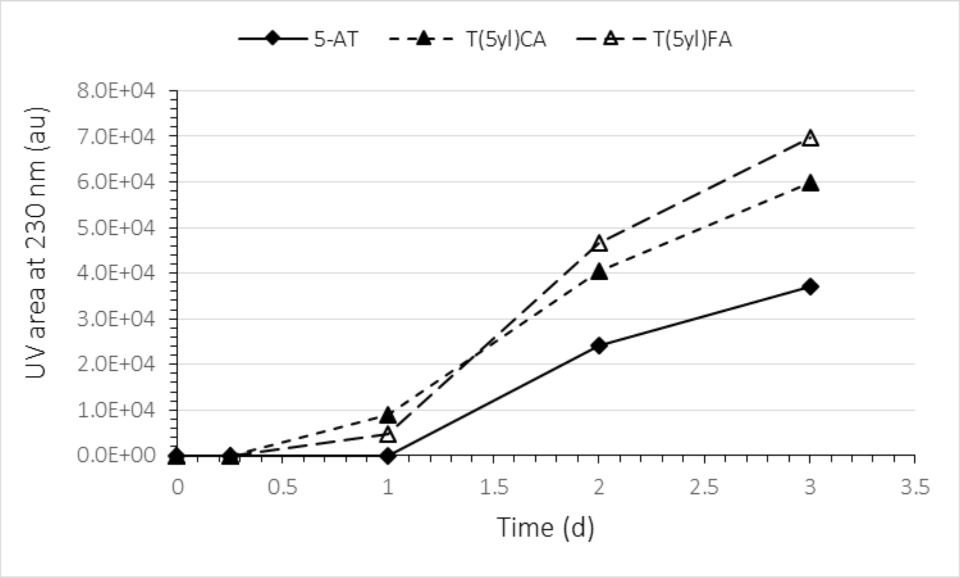

Figure S1. Degradation products of H_2BTA (0.35 mM, pH 3.65) irradiated by simulated sunlight.

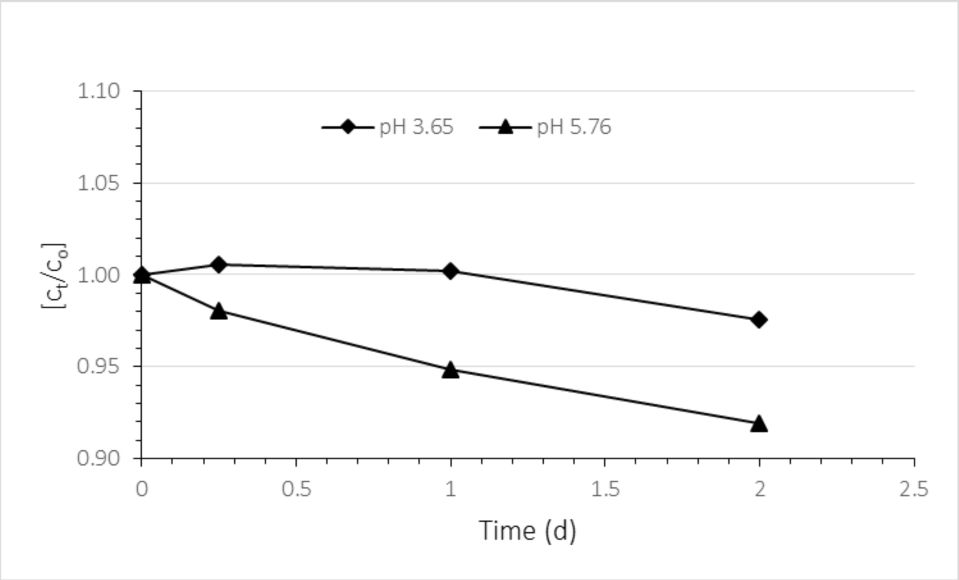

Figure S2. Initial degradation of H_2BTA irradiated in a SolSim reactor at pH 3.65 and pH 5.76. Errors bars of duplicate experiments (< 5%) are not presented.

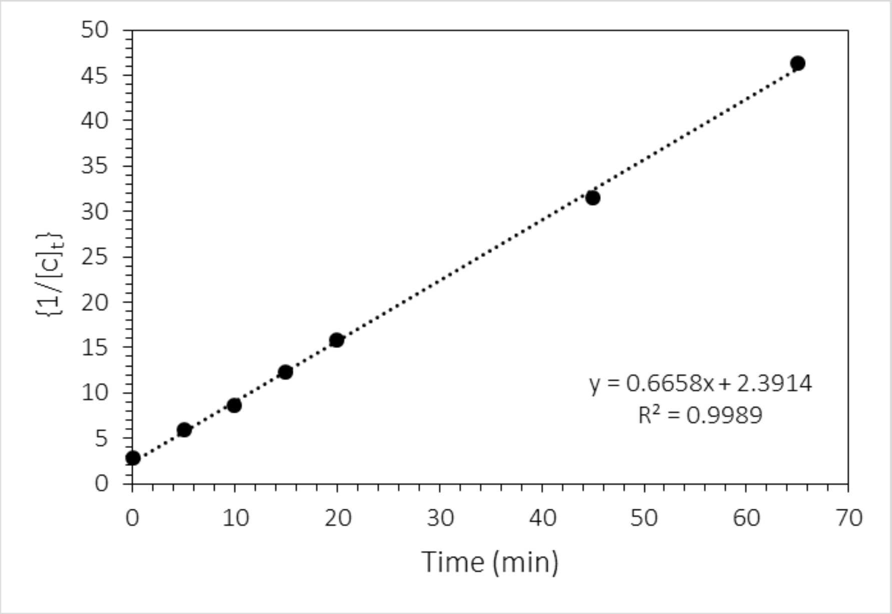

Figure S3. Plot of {1/[c]$_t$} vs time of H_2BTA degradation (0.35 mM in water, pH 3.65) during UV (λ=254 nm) irradiation. RSD of duplicate experiments were less than 5%.

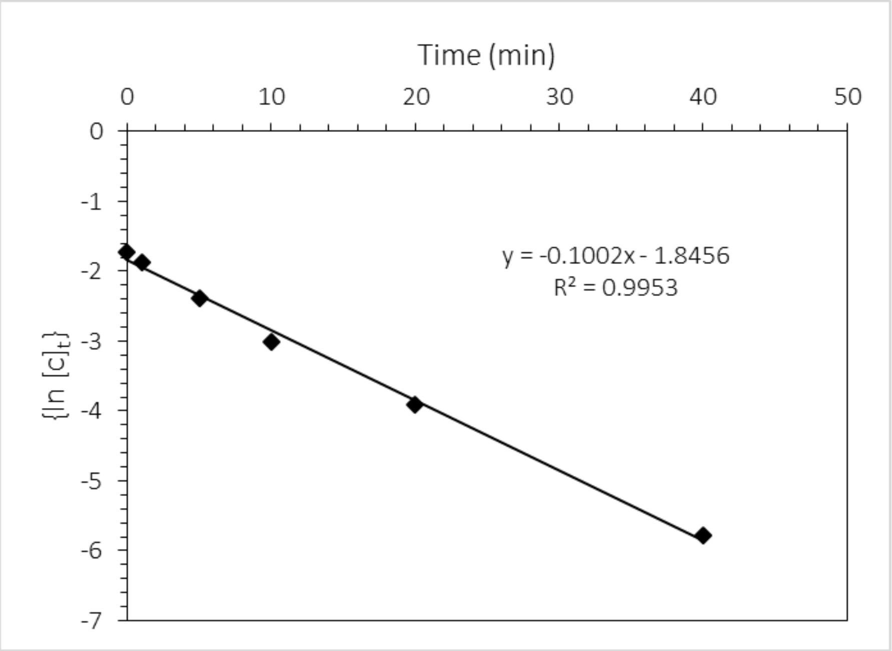

Figure S4. Plot of {ln[c]$_t$} vs time of H_2BTA degradation (0.18 mM in water) during UV (λ=254 nm) irradiation. RSD of duplicate experiments were less than 5%.

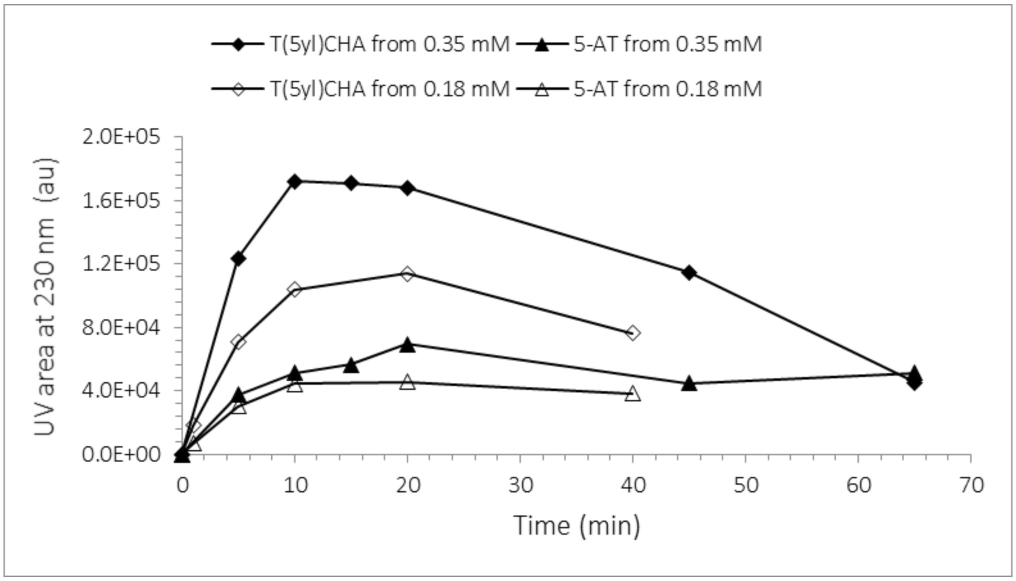

Figure S5. Degradation products of H_2BTA (0.35 mM and 0.18 mM, pH 3.65) photolyzed at λ = 254 nm.

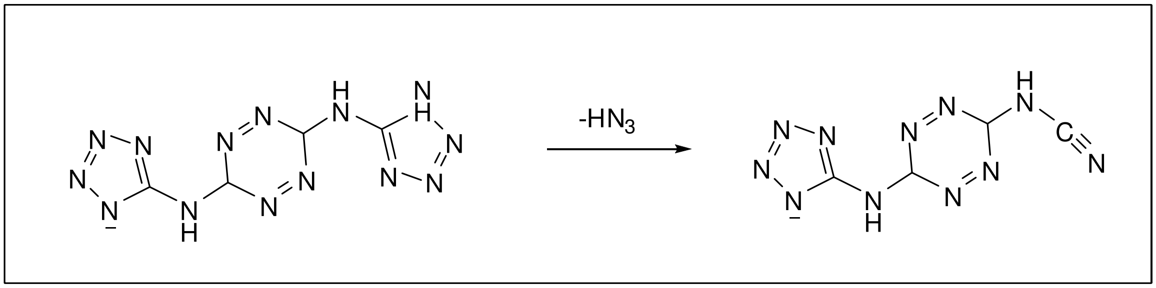

Figure S6. The loss of HN_3 from the anion forms of N3,N6-bis(1*H*-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine proposed by Parvari et al. (2018).