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A combined computational and experimental study of nitrilimines generated from 2,5-substituted tetrazoles

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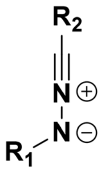
Nitrilimines are useful chemical intermediates for the synthesis of a variety of nitrogen heterocycles for use in pharmaceuticals, energetics, and other energy storage applications. The limitations of these intermediates are explored here with a paired experimental and computational study into the viable substituents for their generation from 2,5-substituted tetrazoles. Nitrilimines generated *via* the loss of nitrogen gas from these tetrazoles are accessible with almost any substitution at the 5-position, with electron withdrawing groups aiding in their formation. The lack of an aryl or heteroaryl substituent at the 2-position of the tetrazole prevented nitrilimine formation in all experiments, an observation that was supported by computation.

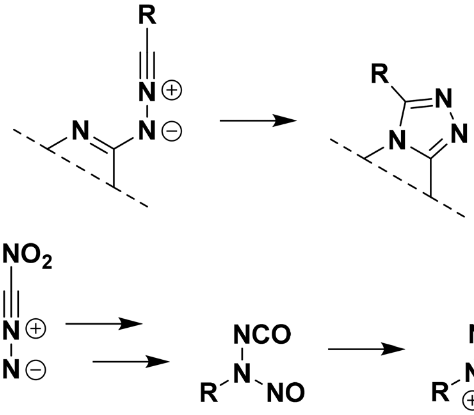
Introduction

Nitrogen-rich materials play a crucial role in the chemical sciences with applications in pharmacology,[1–5] defence,[6–8] mining,[9] and more.[10–15] A number of high nitrogen materials find use in more than one field, such as nitroglycerine, a powerful explosive used to tunnel mountains and a vasodilator used to treat anginal chest pain.[16] In many cases, the primary difference between a pharmaceutical and a high-powered explosive material with the same heterocyclic backbone is the substitution on the backbone. For example, the hexaazaisowurtzitane cage is a nitrogen-rich backbone found in the highly explosive CL-20 as well as in non-narcotic analgesic drugs.[17]

Nitrilimines (Scheme 1) are highly reactive chemical intermediates used in the synthesis of nitrogen-rich materials. They have been used to synthesize triazolopyrazines[18,19] and pyridines[20] through intramolecular cyclization of the nitrilimine with a ring nitrogen atom (Scheme 2). A special intramolecular cyclization occurs when the carbon of the nitrilimine is substituted with a nitro group ($R_2 = NO_2$), resulting in the formation of azasydnones (Scheme 2).[21] These intramolecular rearrangements are believed to proceed *via* *N*-nitroso-*N*-isocyanate intermediates.[22]



Scheme 1 General structure of a nitrilimine intermediate.



Scheme 2 Cyclization of nitrilimines with heteroaryl nitrogen atoms (top) and the cyclization of azasydnones from *C*-nitro nitrilimines (bottom).

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Nitrilimines that are unable to undergo intramolecular cyclization or rearrangement have been found to undergo cycloadditions.[23–29] The most common nitrilimine used for this purpose is diphenyl nitrilimine, which finds use in the synthesis of some pharmaceuticals and antimicrobials.[20] Nitrilimines generated without the capacity for intramolecular reaction or in the absence of substrates to react with are known to dimerize into substituted 1,2,4,5-dihydrotetrazenes (Scheme 3).[30] The generation of diphenyl nitrilimine from 2,5-diphenyltetrazole as well as its structure and reactivity have been studied in great detail.[31–34]

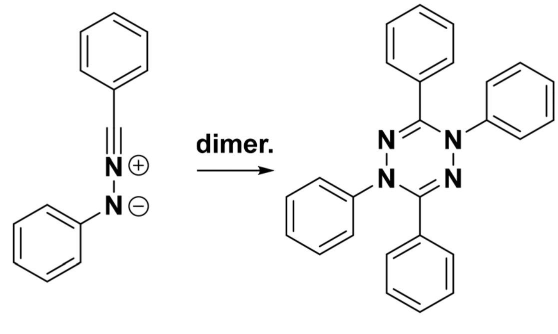
A better understanding of the effects of substitution on the generation of nitrilimines from 2,5-substituted tetrazoles opens the door to the synthesis of many new heterocyclic compounds. In this study, an investigation of the generation and reactivity of nitrilimines from 2,5-substituted tetrazoles is discussed and computational conclusions are backed by experimental findings.

Results and discussion

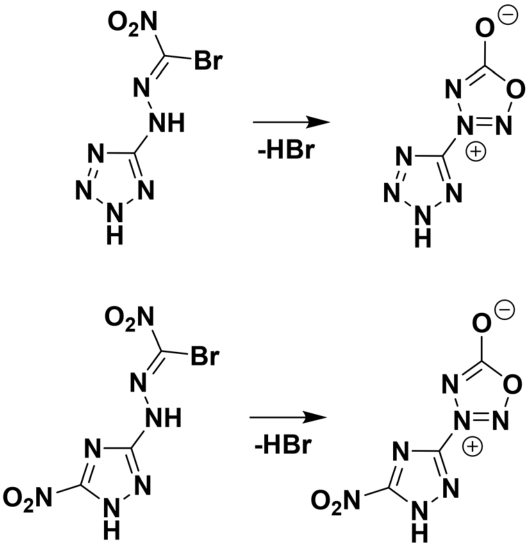
Experimental findings

Our previous work involving nitrilimines[18,21,22,35–37] focused on nitrilimines with *N*-substituted heterocycles. Azasydnones have been synthesized from an appropriate hydrazone *via* generation and subsequent rearrangement of a *C*-nitro nitrilimine with loss of hydrobromic acid (Scheme 4). Conversely, triazolopyrazines were synthesized *via* nitrilimine intramolecular cyclization (Scheme 5). The nitrilimines were generated by irradiating the corresponding tetrazoles with 254 nm centred UV light at room temperature overnight in deuterated acetonitrile.

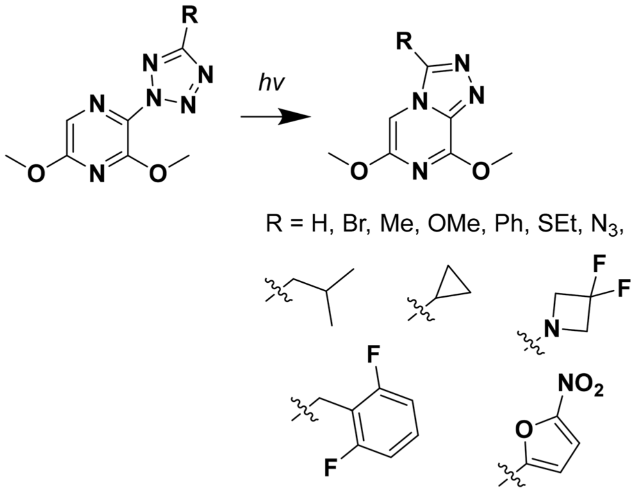
A series of target azasydnones that hypothetically could be accessed through nitrilimine rearrangements from parent tetrazoles were theorized (Scheme 6). The appropriate tetrazoles were synthesized and dissolved in deuterated acetonitrile. Following our previous procedure for nitrilimine generation from tetrazoles, these molecules were irradiated with 254 nm centred UV light overnight at room temperature. In each case, no colour change was observed nor evidence of nitrogen gas release. NMR analysis concluded that the starting materials were still present with no impurities. This process of overnight irradiation and NMR analysis continued until each sample had received over 100 hours of irradiation with no change. The materials were irradiated with 365 nm centred UV light at room temperature overnight and analysed by NMR each morning for an additional 100 hours. The lack of reactivity for the tetrazoles in Scheme 6 suggests that generation of nitrilimines from a 2,5-substituted tetrazole requires aryl or heteroaryl substitution on the nitrogen site.



Scheme 3 Dimerization of nitrilimines into tetrazenes.



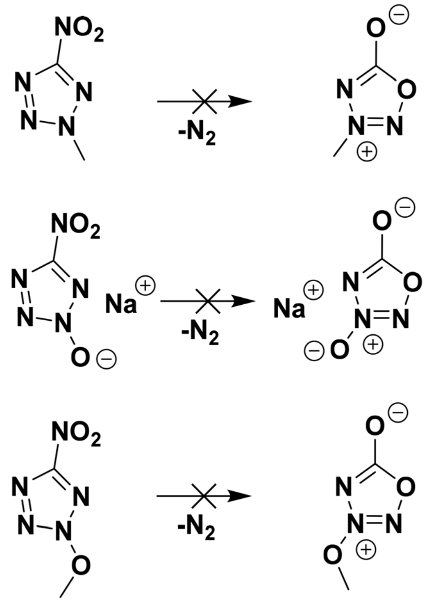
Scheme 4 Azasydnones synthesized *via* nitro-nitrilimine rearrangement.



Scheme 5 Triazolopyrazines synthesized *via* intramolecular rearrangement of nitrilimines.

Initial computational work

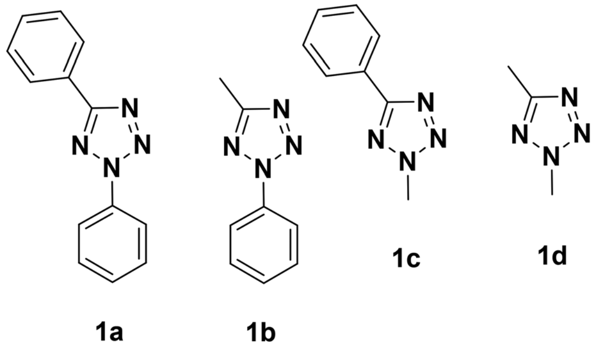
DFT calculations were used to study the retro-[3 + 2] cycloaddition that forms nitrilimines from 2,5-substituted tetrazoles *via* the loss of nitrogen gas; they were performed for a



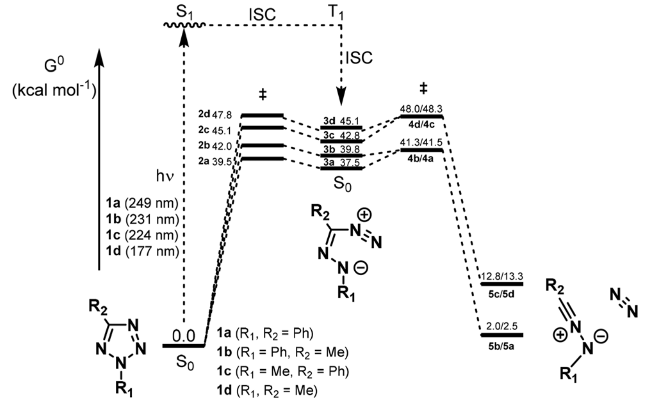
Scheme 6 Theorized target nitrilimine rearrangements.

few model tetrazoles with 2,5-diphenyltetrazole and its nitrilimine as a control because of their large existing body of literature (Scheme 7). This conversion was a good choice of benchmark for feasibility because the conversion of 2,5-diphenyltetrazole to the diphenyl nitrilimine proceeds rapidly with UV irradiation, even at 12 K.[33] The results of this study are summarized in Scheme 8.

Dissociation occurs through a weakly bound intermediate **3**. The reaction out of the intermediate is dependent on the substitution pattern. For the tetrazoles with phenyl substitution on the 2-position (**1a** and **1b**), the energies of the intermediate states were calculated to be 37.5 and 39.8 kcal mol^{-1} for **3a** and **3b**, respectively. The energy of **3c** was approximately +5 kcal mol^{-1} at 42.8 kcal mol^{-1} and **3d** was approximately +8 kcal mol^{-1} at 45.1 kcal mol^{-1} when compared to the control (**3a**). Interestingly, the barriers between the intermediate state **3** and the final nitrilimine **5** were nearly identical for 2-phenyl materials (41.3 and 41.5 kcal mol^{-1} for **4b** and **4a**, respectively) and 2-methyl materials (48.0 and 48.3 kcal mol^{-1} for **4d** and **4c**, respectively), respectively. Similarly, the calculated energies of the final nitrilimines were close for 2-phenyl *versus* 2-methyl nitrilimines. The final state energies for **5a** and **5b** were 2.5 and 2.0 kcal mol^{-1}, respectively, and 12.8 and 13.3 kcal mol^{-1} for **5c** and **5d**, respectively. Nitrilimines generated without *C*-aryl substitution were calculated to have a greater than 10 kcal mol^{-1} increase in energy when compared to those with *C*-aryl substitution.



Scheme 7 Tetrazoles considered for an initial DFT study into the necessity of aryl substitution at the 2-position of tetrazoles used for nitrilimine generation.



Scheme 8 Calculated Gibbs free energies of the model tetrazoles evolving nitrogen gas to produce their corresponding nitrilimines.

These results indicate that nitrilimine generation is significantly less favourable when the nitrogen position is alkyl rather than aryl. Both the intermediate states and final nitrilimines of the alkyl nitrogen systems had energies that were significantly higher than their aryl nitrogen counterparts. Notably, there was very little difference between the final energies of the aryl nitrogen systems and alkyl nitrogen systems, suggesting that the carbon substitution may not play as crucial a role. This study supported the hypothesis that *N*-aryl nitrilimine formation may be generally more feasible than that of the *N*-alkyl.

The π–π* (S_0–S_1) transition *via* chromophore elongation and subsequent intersystem crossing to the triplet state (T_1) which returns to S_0 at surface **3** is facilitated by UV light.[33] For **1a–1d**, the wavelength of light that facilitates the initial π–π* (S_0–S_1) transition was calculated (Scheme 8). These wavelengths fell in the range of 177 nm (**1d**) to 249 nm (**1a**). These calculated wavelengths helped to explain why 254 nm centred UV light was most effective for nitrilimine generation in our previous work.

Further computational work

Another set of calculations were performed to observe the effects of other substitutions on the energy requirements for the loss of nitrogen gas from the tetrazole ring. These calculations were performed such that considerations about intramolecular cyclization could be included when possible (see Further computational work: intramolecular cyclization). The

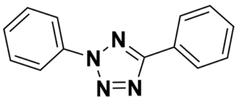
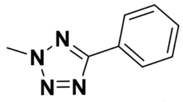
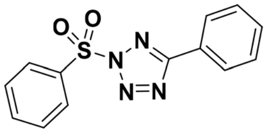
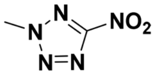
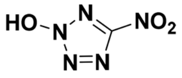
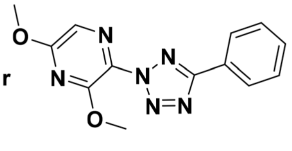
2,5-diphenyltetrazole reference point had a calculated enthalpy for nitrogen loss of 7.1 kcal mol^{-1} (up from 2.5 kcal mol^{-1}) under this setup (Table 1). **1c** had a much smaller shift from 12.8 kcal mol^{-1} to 13.6 kcal mol^{-1}.

1c, **1j**, and **1k** failed to produce nitrilimines experimentally. This was understandable for **1c** and **1j** whose calculated enthalpy for nitrogen loss was appreciably greater than that for the reference at 13.6 and 11.6 kcal mol^{-1}, respectively. Interestingly, **1k** was calculated to have an enthalpy for nitrogen loss of −1.8 kcal mol^{-1}, around 9 kcal mol^{-1} more favourable than the reference, despite failing experimentally. It was decided that this discrepancy was likely due to the presence of the nitro group and that **1k**'s enthalpy for nitrogen loss would realistically lie in a similar range to **1j** (11.6 and kcal mol^{-1}) due to their molecular similarity.

Strong electron withdrawing groups at the nitrogen position appeared to favour nitrogen loss as was seen with **1e**, **1i**, and **1f** (−4.8, −6.6, and −14.2, respectively). Interestingly, **1g** was calculated to have an enthalpy for nitrogen loss of −6.0 kcal mol^{-1}. This outlier could not be synthesized for experimental testing.

For **1m** and **1n**, the swapping of the 5-position for hydrogen or bromine, respectively, had little impact on the calculated enthalpy for nitrogen loss (8.1 and 7.7 kcal mol^{-1}, respectively) compared to the reference (7.1 kcal mol^{-1} for **1a**). This suggested that the carbon substitution is not as important as the nitrogen substitution, a result that was similar in the initial computations. Interestingly, the swapping of a phenyl at the 2-position with a heterocycle significantly reduced the calculated enthalpy for nitrogen loss to 2.3 kcal mol^{-1} for **1h**, 0.3 kcal mol^{-1} for **1q**, and 0.2 kcal mol^{-1} for **1r**. This suggested that heterocycles increased the favourability of nitrogen loss when substituted at the 2-position. For **1o–1q**, the swapping of the phenyl group at the 5-position had a much greater effect on the favourability of nitrogen loss. **1q** (0.3 kcal mol^{-1}) decreased in favourability from **1o** (3.1 kcal mol^{-1}) to **1p** (4.1 kcal mol^{-1}). Each of these, however, was still more favourable than their 2-phenyl counterparts (**1m**, **1n**, and **1a** for **1o–1q**, respectively), further supporting that heterocycles increased favourability.

Table 1 Calculated enthalpies for nitrogen loss from a series of 2,5-substituted tetrazoles and their experimental feasibility

		Enthalpy for N_2 loss [kcal mol^{-1}]	Experimentally feasible [yes/no]
1a		7.1	Yes
1c		13.6	No
1i		−6.6	[a]
1j		11.6	No
1k		−1.8	No
1r		0.2	Yes

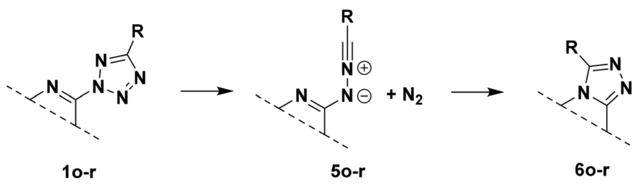
[a] Experimentally known; however, it is not made *via* the tetrazole route.[38]

Further computational work: intramolecular cyclization

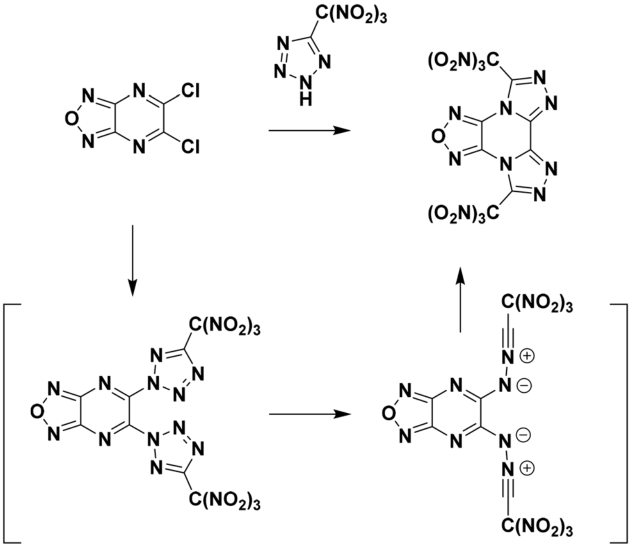
As discussed in the Introduction, the presence of a vicinal ring nitrogen to a *C*-substituted nitrilimine offered the potential for intramolecular cyclization (Scheme 9). For these examples, a cyclization transition state enthalpy barrier and final cyclization enthalpy were calculated (Table 3).

As discussed previously, the enthalpies for nitrogen loss for **1o–1r** were much lower than that of reference **1a** (7.1 kcal mol^{-1}), implying that nitrilimine generation is favoured. In each case, the calculated barrier to cyclization was surpassed significantly by the calculated enthalpy of cyclization (Table 3). Interestingly, **1q** and **1r** had the same calculated cyclization enthalpy of −33.2 kcal mol^{-1} despite having different heterocycles at the nitrogen position. This implied that cyclization enthalpy is controlled by the carbon substitution rather than the nitrogen substitution. This was the opposite of what was observed for the calculated enthalpy of nitrogen loss where the nitrogen substituent had the largest effect. The less sterically hindering carbon substituents of hydrogen and bromine (**1o** and **1p**, respectively) had more favourable cyclization enthalpies (−38.4 and −40.6 kcal mol^{-1}, respectively) than the phenyl substituted materials (−33.2 kcal mol^{-1} for both **1q** and **1r**). Despite these differences, the calculated enthalpies for cyclization were favourable by greater than 30 kcal mol^{-1}. Although no meaningful trend could be elucidated for the calculated enthalpies for the cyclisation barriers, each appeared to fall within a similar range between 7 and 10 kcal mol^{-1}.

These results agreed with our previous work in which numerous examples of successful nitrilimine generation and intramolecular cyclization of tetrazoles substituted at the 2-position with 2,6-dimethoxypyrazine were reported (Scheme 5).[18] Another study on nitrilimine intramolecular



Scheme 9 Outline for nitrilimine generation and subsequent intramolecular cyclization.



Scheme 10 The cyclization of two nitrilimines on a pyrazine backbone.

cyclization supported our results: the cyclization of 2,3-di(5-trinitromethyltetrazole-2-yl)pyrazinofurazan into its corresponding tri-annulated pyrazine (Scheme 10).[39] After 2 hours at room temperature, the coupling reaction of 5-trinitromethyltetrazole with 2,3-dichloropyrazinofurazan had fully formed the tetracycle. This work supported our findings about the presence of electron withdrawing groups and heterocycles at the 2-position of tetrazoles favouring nitrilimine generation.

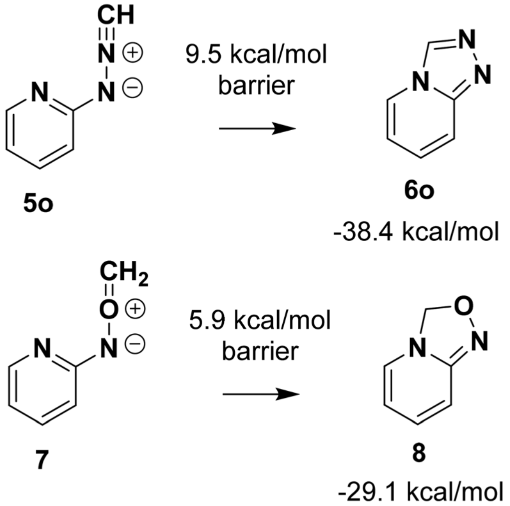
Additional considerations

Nitrilimines could be thought of as nitrile-trapped nitrenes. The cyclization of such a system is modelled by **5o** (Scheme 11). This was compared to a similar formaldehyde-trapped nitrene (**7**). The calculated cyclization barrier for the nitrile-trapped nitrene (nitrilimine) was 9.5 kcal mol^{-1} and its cyclization enthalpy was −38.4 kcal mol^{-1}. The cyclization barrier for the formaldehyde-trapped nitrene **7** was 5.9 kcal mol^{-1} and its cyclization enthalpy was −29.1 kcal mol^{-1}. Although the calculated cyclization barrier was greater for the nitrilimine, the calculated cyclization enthalpy was much more favourable than that of the hypothetical formaldehyde analogue. This was understandable, since the nitrilimine cyclization formed a planar annulated system.

Experimental

All chemicals were used as purchased from Ambeed, Sigma Aldrich, or Fisher Scientific without further purification. NMR analysis was conducted using a Bruker AV-III 500 MHz NMR spectrometer. UV light was supplied by a benchtop UV lamp source for TLC monitoring.

2-Methyl-5-phenyltetrazole,[40] 5-nitro-2-methyltetrazole,[41] and 5-nitrotetrazole-2-oxide[42] were synthesized according to literature procedures.



Scheme 11 Comparison of nitrilimines to their hypothetical formaldehyde-trapped nitrene analogues.

2-Methoxy-5-nitrotetrazole

1.80 g (7.57 mmol) of silver nitrotetrazolate-2*N*-oxide was slurried in 100 ml of acetone. To this was added 5.65 ml (90 mmol) of methyliodide and the suspension was stirred overnight in the dark. The solution was then filtered to remove precipitated silver iodide, and the filtrate was evaporated under ambient conditions, yielding 1.07 g (97%) of 2-methoxy-5-nitrotetrazole.

General method for generating nitrilimines from 2,5-substituted tetrazoles

The general method for the nitrilimine generation was a modified version of the method used by Yount *et al.*[18] A sample of the 2,5-substituted tetrazole was dissolved in deuterated acetonitrile and ^{1}H and ^{13}C spectra were acquired. The sample was then exposed to 100 hours of 254 nm UV light and was checked by ^{1}H and ^{13}C NMR every 24 hours followed by 100 hours at 365 nm UV light with a similar NMR checking procedure. No change in the NMR spectra over the combined 200 hours of UV exposure paired with no generation of nitrogen gas bubbles indicated that no reaction occurred.

2-Methyl-5-phenyltetrazole (1c). No reaction.

2-Methyl-5-nitrotetrazole (1j). No reaction.

2-Methoxy-5-nitrotetrazole. No reaction.

5-Nitrotetrazole-2-oxide (1k). No reaction.

3,5-Dimethoxy-2-(5-phenyl-2*H*-tetrazole-2-yl)pyrazine (1r). It successfully produced the nitrilimine as evidenced by a 61.5% yield of 6,8-dimethoxy-3-phenyl-[1,2,4]triazolo[4,3-*a*]pyrazine (**6r**).[18]

Computational work

Initial computational work (Scheme 8):

DFT calculations were performed at the cam-B3LYP/def2-TZVP, CPCM = acetonitrile level of theory to investigate the preparation of nitrilimines *via* photochemical retro-[3 + 2]

Table 2 Calculated enthalpies for nitrogen loss for an expanded series of 2,5-substituted tetrazoles

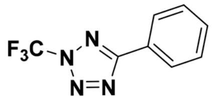
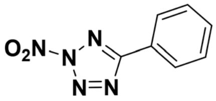
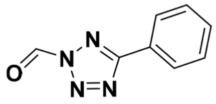
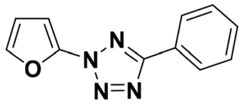
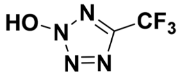
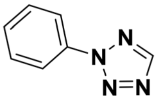
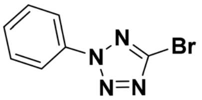
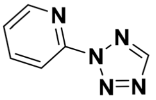
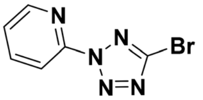
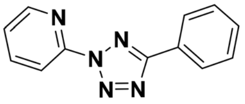
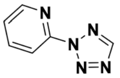
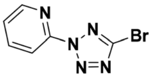
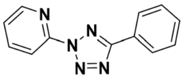
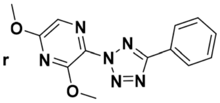
		Enthalpy for N_2 loss [kcal mol^{-1}]
1e		−4.8
1f		−14.2
1g		−6.0
1h		2.3
1l		11.9
1m		8.1
1n		7.7
1o		3.1
1p		4.1
1q		0.3

Table 3 Enthalpies for generation of nitrilimines, cyclization barriers, and cyclization of eligible materials

		Enthalpy for N_2 loss [kcal mol^{-1}]	Cyclization barrier [kcal mol^{-1}]	Cyclization enthalpy [kcal mol^{-1}]
1o		3.1	9.5	−38.4
1p		4.1	7.6	−40.6
1q		0.3	8.8	−33.2
1r		0.2	9.6	−33.2

cycloaddition of 2,5-substituted tetrazoles. Input files were prepared locally using GaussView 6.0, Gabedit 2.5.1, and Notepad++, and transferred to the University of Pennsylvania General Purpose Cluster (GPC) where calculations were carried out in Orca 5.0.3[43] using the Gaussian 16[44] suite of programs.

Later computational work (Tables 1–3):

The loss of nitrogen gas to produce nitrilimines and, where appropriate, the transition states and final products of intramolecular cyclizations were studied in the gas phase. The optimized structures, frequencies, electronic energies, and 298 K enthalpies for all tetrazoles, nitrilimines, cyclization transition states, and cyclic products were calculated at the B3LYP/6-311+G(3df,2p) level of theory.

Conclusions

In conclusion, a better understanding of the effects of substitution on the generation of nitrilimines from 2,5-substituted tetrazoles would improve experimental design and guide future target materials. Experimental results indicated that tetrazoles with aryl or heteroaryl substitution at the 2-position made nitrilimine generation favourable, while alkyl substitution resulted in no reaction. Computational results agreed with these observations and expanded on them. Heteroaryl substitutions increased the favourability of nitrilimine generation with a greater increase in favourability from nitrogen heterocycles.

Computational studies predicted that strong electron withdrawing groups would strongly favour nitrilimine generation. The results did not agree with experimental results except when the 2-position of the tetrazole was an aryl or heteroaryl substituent.

The cyclization of nitrilimines with vicinal ring nitrogen atoms was to be experimentally facile. Computational studies predicted similarly, with bulkier carbon substituents being less favourable than less sterically hindered substituents.

Overall, the experimental and computational study indicated that nitrilimine generation from 2,5-substituted tetrazoles was hindered by a lack of aryl or heteroaryl substitution at the 2-position. When substituted aptly, heteroaryl and electron withdrawing substituents further favoured nitrilimine generation, with nitrogen heterocycles being more favourable, and the intramolecular cyclization of nitrilimines with nitrogen heterocycles was highly favourable.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: Table S1 and all computational coordinates and energies for calculated structures/surfaces. See DOI: https://doi.org/10.1039/d6dt00045b.

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