

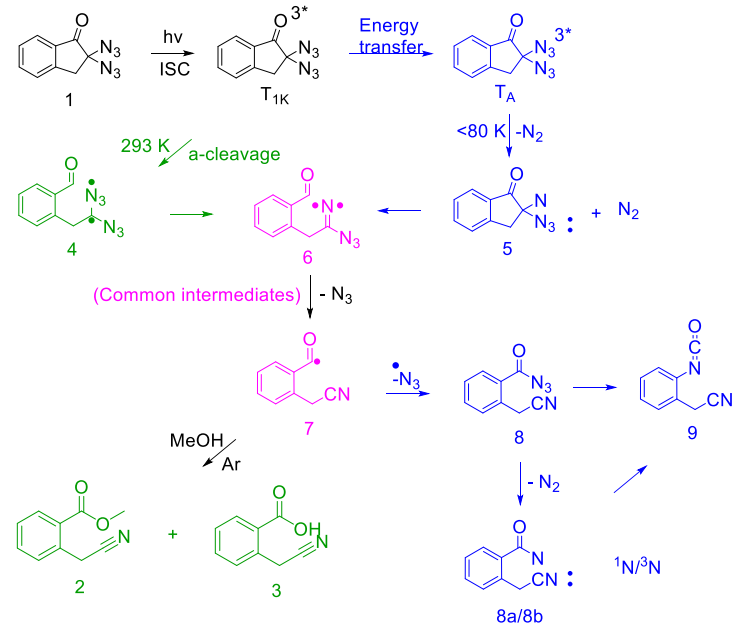
As part of my research, I piloted interdisciplinary studies toward understanding how to make safer sunblockers and explosives. My work has:

- Explicated sustainable pathways by using low-energy light (LEDs) sources as a traceless reagent to initiate reactions.
- Collaborated with UC College of Pharmacy to understand rheological and formulation techniques for sunscreen study that contributed to one manuscript.
- Spearheaded 2 peer-reviewed publications highlighting the temperature-controlled reaction pathway of a triplet-sensitized alkyl azide and safe photo-explosivity of *o*-nitroaryl azides reaction after denitrogenation, respectively.

With my diverse expertise, I hope to use my relational skills within interdisciplinary teams to supply direct and witty resolutions to mechanical and nontechnical tasks.

A. Elucidating the Mechanism for Forming Isocyanates from a Geminal Alkyl Diaze

Alkyl azides are versatile building blocks in synthetic applications involving click reactions and metal-free formation of C-N bonds. Discovering new usage of photoreactive alkyl azides requires an improved understanding of their complex reaction mechanisms, which depend on three main factors including azide structure, irradiation wavelength, and absorption of light either through directly or with sensitizers. These particular azides concertedly rearrange to form an imine faster than achieving the singlet excited state.¹⁻³ By designing a molecule with a built-in triplet sensitizer, the singlet excited state is achievable and optimizes the singlet-triplet energy gap allowing for efficient intersystem crossing (ISC) to form triplet ketone species **T_{1K}**.



Scheme 1. Proposed mechanism of 2,2-diazido-2,3-dihydroinden-1-one **1** in room (green) temperature and cryogenic temperatures (blue).

Overall, different reactivity was observed in solution and matrices. The proposed mechanism (Scheme 1) identifies all mechanistic pathways of **1**. By adjusting the reaction conditions with temperature, formation of triplet alkyl nitrene plus irreversible N_2 gas release was favored over reversible α -cleavage. Minimizing the diffusion around **1** allowed us to identify and assign secondary product formation to **9**, which has a known precursor of acyl azide **8** via Curtius rearrangement.¹⁵ Similar ¹⁵N isotopic labelling experiments were conducted to help us determine presence of **8** while assigning peaks to both the acetophenone and azido moieties. This project laid the groundwork for temperature-controlled sustainable synthesis of photoreactive compounds.

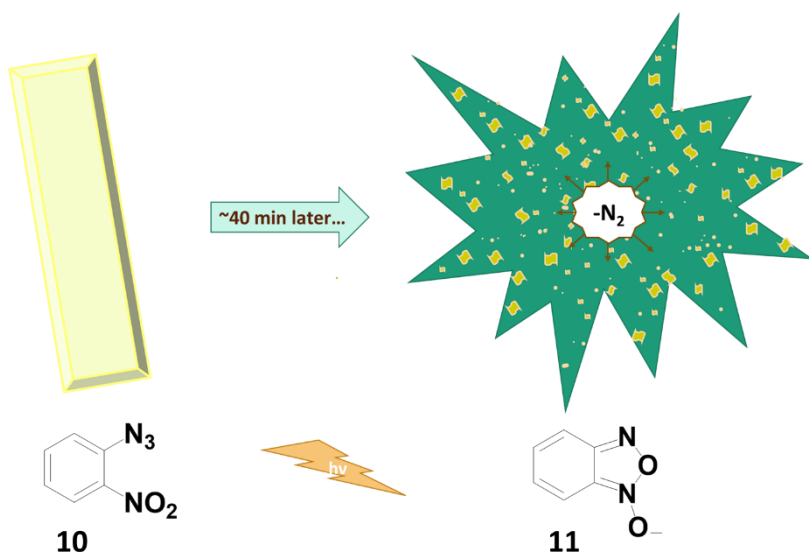
B. Investigation of the correlation between gas-releasing crystals and how the crystal lattice controls crystalline motion using *o*-nitrophenyl azides.

Photodynamic organic crystals have potential in applications such as robotics, sensors,⁵ and actuators⁶ due to their various types of macroscopic behavior once stimulated. These crystals can exhibit photodynamic effects as deformation, motion, and disintegrative effects, which can be categorized as regular and stochastic motions, respectively.⁷⁻⁸ More

specifically, gas release crystals⁷ are interesting due to their potential applications towards making safer explosives and nanopropulsion devices.¹⁴ The Gudmundsdottir lab focuses on the photoreactivity of crystalline azido compounds to understand how release of nitrogen gas within the crystals lattice affects their photodynamic response.⁷ Herein, we prepared a high energy density material (HEDM) with two explosophores where mechanism has been studied extensively,⁹⁻¹³ 1-azido-2-nitrobenzene **10**, and investigated its photodynamic response upon irradiation. We believe we are the first to report its photo-explosive dynamics.

X-ray crystallography was performed to analyze crystal packing and make hypotheses on macroscopic motion of **10**. Single crystals of azides **10** were grown from an ethyl acetate/hexane solution at 0 °C. Reactivity was promptly recorded upon photolysis ($\lambda_{\text{irrad}} = 400\text{-}700\text{ nm}$; LED) on the stage of a Keyence VHX-7000 digital microscope. A single crystal of **10** ($\sim 0.8 \times 0.2\text{ mm}$) lost transparency and uniformly dispersed by explosion over two times the distance of original crystal within ~ 40 minutes. The energetics of the framework of **10** were probed by calculations to gain insight to where the crystals are most likely to deteriorate using CrystalExplorer17 software. We examined the lattice interactions and identified stronger ($27.4\text{-}39.8\text{ kJ mol}^{-1}$) and weaker ($6.6\text{-}10.9\text{ kJ mol}^{-1}$) intermolecular forces (IMFs).

In summary, I proposed that the weaker forces in the lattice in the *c*-axis are broken upon the cyclization to form benzofuroxan **11** with minimal movement ($\varphi = 37^\circ$) and expulsion of nitrogen gas. A similar study correlating crystal disintegration induced by gas release has been reported in 2020 by Shields *et. al.*⁷ where photomechanical effects are



associated with degradation in an ordered structure of a compound's unit cell. This chemical reaction resulted in no change in space group (*P*-1, triclinic) as N_2 gas fills and strains the lattice forces. This is interesting as change in lattice structure from reactant to product is one of many driving forces of dynamic responses. While being the first to report its uniform photo-explosivity ($\sim 4\text{ }\mu\text{g}$, $\sim 1\text{ cm}$ blast radius) in under 40 minutes, this work laid the basis for making safer explosives initiated by light. Future work consists of adding an explosophore ($-\text{NO}_2$) to the *o*-nitrophenyl azide to fundamentally understand the differences in the photomechanical effects without changing the photochemical reaction in hopes to learn their usefulness in potential applications.

Figure 1. Graphical abstract of the denitrogenation of 1-azido-2-nitrobenzene.

C. Future Proposal

I am interested in the photochemistry of short and long-lived, unique nitrogen radical intermediates and pathway to product formation. This research is under the umbrella of physical organic photochemistry with a concentration of developing smart, energetic materials.

Syntheses of new azido precursors allow us to investigate their mechanism in solution, and their photodynamic response on macroscopic level after denitrogenation. Orthodox methods of organic chemistry are involved to help us achieve our goal (synthesis including typical purification methods, analysis of reaction mixtures, isolation and spectroscopic identification of products formed). To directly detect these intriguing molecules, we utilize laser flash photolysis techniques with nanosecond time resolution, matrix isolation spectroscopy and computational chemistry. X-ray diffraction and video microscopy are used to observe the macroscopic motions exhibited.

The goals are to understand and influence mechanistic pathways of organic azides to test photochemical theories, to recognize the interactions of reactive intermediates with solvents, and in the solid-state intramolecularly within its lattice. Because these compounds contain explosophores, we intertwine safety measures into our procedures and follow these diligently. This research exemplifies interdisciplinary studies and highlights diversity for numerous reasons. I hope to introduce this research to many intelligent undergraduates at my future teaching institution and several nearby high schools interested in STEM fields. On top of strong technical skills, they will continue to learn strong soft

skills such as effective scientific communication by asking the right questions, time management, and taking ownership of their work. This work will continue to touch inspired minds across the nation. Firstly, I will diligently write grants to financially support this research. The future James Lab hopes to continue sharing the importance of this work and keep innovation alive while safely exploring explosives.

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