Photochemical Cycloadditions of Organic Crystals: Shedding Light on Solid-State Reactivity

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Investigating solid-state reactivity dates back to the early 1900s when organic chemists routinely worked with solid materials due to the lack of suitable solvents.[1] Although solid phase reactions were observed as early as 1918, the field remained stagnant until a greater understanding of crystallography developed.[2] It was not until the 1960s that a systematic study to probe solid-state reactivity of olefins was performed by G. M. J. Schmidt.[3] Extensive experiments on the photodimerization of crystalline cinnamic acid derivatives revealed specific lattice requirements governing reactivity and provided key insight into the nature of solid phase reactions.[3] This pioneering work proved to be the benchmark of the field for another 30 years and paved the way for modern scientific advancement of photochemical cycloadditions in the solid state.

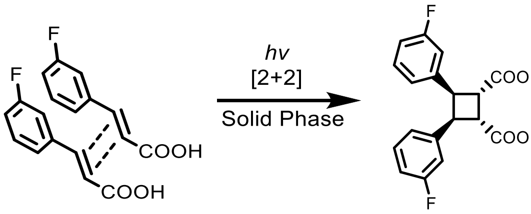

Figure 1: [2+2] Photocyclization of 3-fluoro-*trans*-cinnamic acid.[3]

The experiments performed by Schmidt and coworkers revealed topochemical requirements, or spatial restrictions, on the lattice arrangement necessary to achieve successful dimerization; the most important criterion of which involved the intermolecular distance between potentially reactive double bonds.[3] Schmidt's data suggested that successful transformations require an intermolecular olefin centroid-to-centroid distance of 4.2 Å or less. Additionally, parallel alignment of double bonds in the crystal lattice is paramount for successful photocycloaddition. Although no specific angular limits were outlined, many examples of failed transformations with non-parallel arrangement of double bonds have been reported,[3-6] even with angles between olefins as low as 6°.[6] It is important to note that although these rules rationalized many results, exceptions have been reported in the literature including cases of failed reactions in spite of favorable topochemistry[7] and cases of successful dimerization without adhering to the established topochemical requirements.[8]

Undoubtedly, the most difficult aspect of solid-state photodimerizations lies in achieving a topochemically suitable molecular arrangement. The inability to predict molecular arrangement *a priori* inhibited swift development of photochemical reactions in the solid state.[9] This lack of understanding required scientists to develop methods that induced desired molecular organization and crystal packing, leading to a plethora of recent developments in the literature since the early 2000s.[9-13] "Crystal engineering," or utilizing intermolecular interactions for the rational design of molecular solids,[3] has grown into a rich field of chemistry and provides many possibilities for topochemically allowed solid-state photoreactions. Strategies including π-π stacking,[14] template oriented hydrogen bonding,[15] and coordination complexes[9] have all been reported to induce desired crystal packing. These clever motifs provide opportunities for applications utilizing topochemical photoreactions in the solid state.[13]

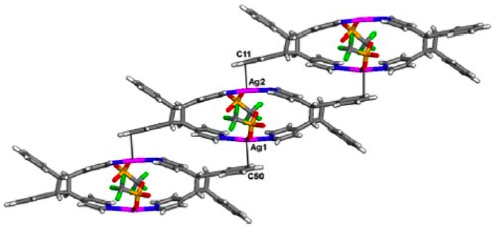

Figure 2: 1D coordination polymer formed after SCSC photodimerization of a 4-styrylpyridine Ag (I) complex.

The MacGillivray group recently employed coordination templating to construct a one-dimensional (1D) coordination polymer built from a π-stacked metal-organic solid that undergoes a single-crystal-to-single-crystal (SCSC) [2+2] photodimerization.[16] The photodimerized 1D polymer exhibits 40% higher conductivity than the non-dimerized product, representing the first example of an increase in conductivity of a solid resulting from a [2+2] cycloaddition.[16] The authors attribute the increase in conductivity to a higher contribution from Ag(I) ions to the valence band in the photodimerized product.[16] These results can be applied to electrical properties of metal-organic frameworks.

The Vittal group recently reported the first instance of the photosalient effect, where an external stimulus induces a sudden and rapid mechanical response, in response to a solid state [2+2] cycloaddition reaction in single crystals.[17] Slow evaporation of a methanol solution of $Zn(NO_3)_2$, sodium benzoate, and 2'-fluoro-4-styrylpyridine (L) yielded yellow block-shaped single crystals of $[Zn_2(benzoate)_4(L)_2]$ with correct topochemical arrangement of olefins for [2+2] cycloaddition in the lattice.[17] Irradiating the crystals with a single UV LED source (λ = 375 nm) initiated the dimerization reaction, forming a 1D polymer and triggering crystal jumping, rolling, flipping, splitting, or explosion.[17] The dimerization process generated phase-heterometry–different amounts of stress in each of the crystal axes–and resulted in an 11% increase in volume of the lattice.[17] As a result of the rapid increase in volume, the crystal releases its stress by undergoing propelled motion.[17] These results directly apply towards designing materials which convert light into mechanical motion and provides an opportunity for alternative energy conversion.

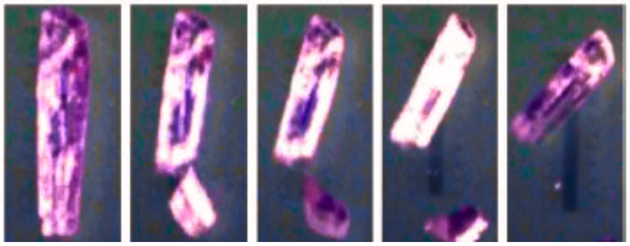

Figure 3: Crystals experiencing propelled motion after UV-induced phase-heterometry.[17]

Other groups have utilized solid-state photochemical cycloadditions to synthesize stereospecific molecules in gram quantities, where the products may be tedious to synthesize in solution phase.[18] Additional applications include construction of 1D coordination polymers,[19] 2D polymers,[14] and metal-organic frameworks.[20] With new insight toward controlled molecular arrangement of crystal lattices, the field of photochemical reactions of organic crystals has seen a resurgence of activity. Recent literature displays the ability to engineer crystals in an *a priori* fashion, alleviating the burden of topochemical restrictions, and providing a simplified approach toward solid-state reactions. Certainly, controlling the crystal packing of molecules is a scientific feat poised to contribute huge insights toward solid-state reactivity. Further investigation on the mechanisms of solid-state cycloadditions will enhance understanding of reaction intermediates and discovering other clever template motifs will increase the application scope in this field.

References

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