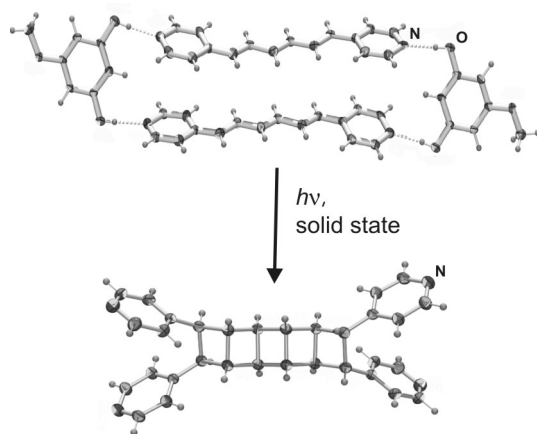


Synthesis of Molecular Ladders in the Solid State,
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Keywords: Molecular Ladders; Solid-state Chemistry;
Linear Templates

Despite the high yields and stereospecificity of topochemical solid-state reactions, the solid state has remained largely unexploited as a medium of organic synthesis, mostly due to difficulties of controlling molecular organization in solids. We are developing a method to control solid-state reactivity using molecules acting as linear templates, such as resorcinol. Co-crystallization of the linear template with reactants, in the form of olefins containing pyridines, results in crystalline solids composed of discrete molecular assemblies, held together by O-H...N hydrogen bonds. The double bonds of the reactants within assemblies are aligned for a stereocontrolled [2+2] photodimerization, allowing the formation of a cyclobutane product in 100 % yield upon UV-irradiation.[1] Exploiting the modular nature of the template-directed solid-state approach, we now extend the scope of the method to the synthesis of molecular ladders, using conjugated polyenes as reactants. Molecular ladders are of interest in theoretical chemistry and nanotechnology, as well as biochemistry. While molecular ladders can, in principle, be obtained *via* sequential [2+2] photodimerization of polyenes[2], such approach has found little practical use, mainly due to the difficulties of positioning reactants. We have recognized resorcinol linear templates as a means to overcome such difficulties. Consequently, co-crystallization of diene, triene or tetraene reactants with resorcinols yielded solids composed of discrete assemblies, as evidenced by X-ray single crystal structure analysis. The double bonds of polyenes within each assembly are aligned for a [2+2] photodimerization.



Upon UV-irradiation, co-crystals of the diene and the triene yield the [3]- and [5]-ladderanes, respectively, in quantitative yields. The final characterization of the products has been accomplished by way of X-ray single crystal structure analysis.[3] Research is now underway to synthesize longer molecular ladders using the template-directed solid-state approach.

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