



# Volume demanding geometric isomerization of *cis*-4-stilbazole. HCl salts in the crystalline state: Probing the role of a metastable dimer



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## ABSTRACT

*Cis*-*trans* isomerization is one of the most common and well-investigated photoreaction of olefins in solution. This occurs via 180° rotation of one of the substituents on C=C bond requiring large space around the double bond. One would expect that in crystals the neighboring molecules would prohibit such a process. In spite of this in early 1960s Schmidt and co-workers reported occurrence of such a process in crystals via 2 + 2 'meta cyclobutane' formation. In this study by examining the photochemistry of four *cis*-stilbazolium salts we show that the photoconversion to the corresponding *trans* isomers does not occur via 2 + 2 addition. Large separation that ensures considerable space between neighboring olefins favors *cis*-*trans* isomerization in crystals. An aspect that is puzzling is that the product *trans* isomer phase separates and recrystallizes within the parent *cis* crystals and photodimerizes to the cyclobutane dimer. Details of this phenomenon are to be understood.

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## 1. Introduction

The sporadic interest for over a century on the photochemistry of organic molecules in the solid state and as host-guest assemblies in solution have intensified during the last five decades [1]. Early studies on light induced reactions performed in the solid state focused mostly on synthesis of new molecules. Recent availability of X-ray diffractometers and powerful computing programs for structure solution has enabled chemists to connect a molecule's crystal packing with their reactivity and probe molecular transformation mechanisms in solids. The topochemical postulate formulated by Schmidt for solid-state photodimerization of *trans*-cinnamic acids, having stood the test of time, has served as the foundation for the development of solid-state photochemistry [2]; the few exceptions to the postulate have helped fine-tune it [3].

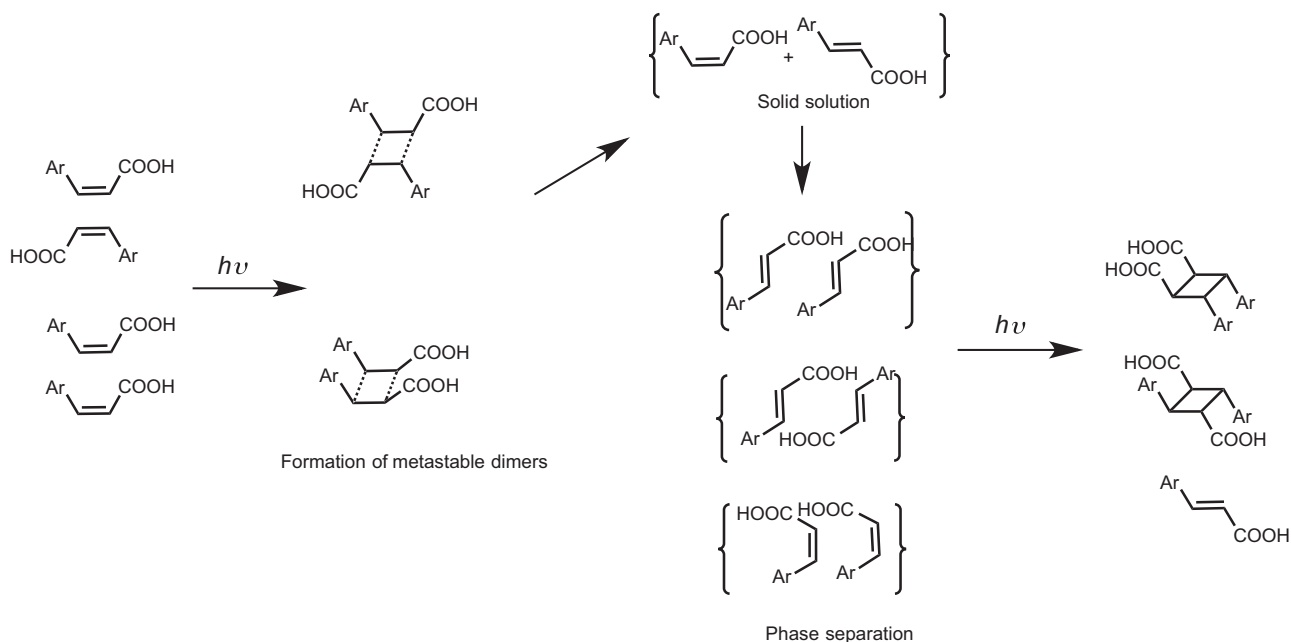
Olefins in general undergo two main reactions in solution: unimolecular geometric isomerization and bimolecular dimerization [4]. Schmidt's attempt to extend the topochemical postulate to *cis*-cinnamic acids led to the observation of geometric isomerization in crystals [5]. Unlike photodimerization, Schmidt's views on light induced geometric isomerization of cinnamic acids in crystals have not been widely accepted with no clear understanding till date of how the *cis*-*trans* isomerization requiring large molecular

motion at least at one end of the C=C bond occurs in the crystalline state. As indicated above *cis*-*trans* isomerization in crystals was a serendipitous discovery. The dimers from excitation of *cis*-cinnamic acids examined by Schmidt and co-workers could only be understood by dimerization of two *trans*-cinnamic acids and not two *cis*-cinnamic acids. To accommodate this anomalous phenomenon Schmidt proposed a *cis*- to *trans* isomer conversion, prompted by interaction of an excited *cis* isomer with an adjacent ground state molecule within a distance of 4.2 Å, to precede dimerization [5]. The 'metastable dimer' thus formed is presumed to be the intermediate that facilitates *cis* to *trans* isomerization. This proposal implied the requirement of <4.2 Å separation of adjacent molecules for *cis*-*trans* isomerization. The proposed mechanism by Schmidt and co-workers illustrated in Scheme 1 involves several steps: the initial formation of a metastable dimer leading to the *trans*-isomer as a solid solution within the *cis* lattice followed by the separation of the *trans*-isomers in a thermally controlled recrystallization step into their own lattice. In the final step the excited *trans* isomer yields the lattice controlled stable dimer.

After almost four decades following the early (1902 and 1923) reports on solid-state photoisomerization of olefins from the laboratories of Paal, Schulze and Rice on dibenzoyl ethylene and benzoylacrylic acid esters [6,7], Schmidt and co-workers reported their results on the geometric isomerization of *cis*-cinnamic acids [5,8]. This report prompted several studies focusing on the mechanism of *cis*-*trans* isomerization in crystals [9–16]. Currently four mechanisms exist, including the original suggestion by

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**Scheme 1.** Proposed consolidated mechanism for the *cis-trans* isomerization of *cis*-cinnamic acids in crystals.

Schmidt, to rationalize the *cis-trans* isomerization in crystals: (a) isomerization via a metastable dimer intermediate, (b) conventional one bond (C=C) rotation, [17,18] (c) two bond rotation of adjacent single and double bonds (Hula twist) [19–22], and (d) bicycle pedal mechanism involving concurrent isomerization of more than one double bond [23–26].

A few examples of *cis-trans* isomerization where the adjacent C=C bonds are separated by more than 4.2 Å have also been reported since Schmidt and co-workers' report casting doubt on the role of a metastable dimer during *cis-trans* isomerization [17,18,27–29]. This prompted us to ponder the importance of metastable dimer and probe the generality of it as an intermediate during *cis-trans* isomerization. In this context we have currently examined the excited state behavior of four *cis*-stilbazole. HCl salts **1b–4b** (Scheme 2) where the adjacent C=C bonds were separated by >5.5 Å (see discussion below). Such a long distance of separation should prevent metastable dimer formation. To examine the second part of the reaction namely the *trans* isomer, formed from the *cis* isomer, yielding the dimer by recrystallizing in the lattice of the *cis*-isomer we turned to our recent finding that excitation of hydrated *trans*-stilbazole.HCl salts (**5b–8b**) resulted in [2+2] cycloaddition to yield a *anti*-head-tail dimer [30,31]. Thus, *cis*-stilbazole.HCl salts **1b–4b** seemed ideal to test whether the corresponding *trans*-stilbazole. HCl salts formed in the *cis* lattice would dimerize. Finally, if metastable intermediate is not involved, identification of a pre-requisite condition for *cis-trans* isomerization in crystals is important. With these in mind we carried out a combined X-ray crystallographic and photochemical study of four

*cis*-stilbazole.HCl salts (**1b–4b**) shown in Scheme 2 whose results are presented below.

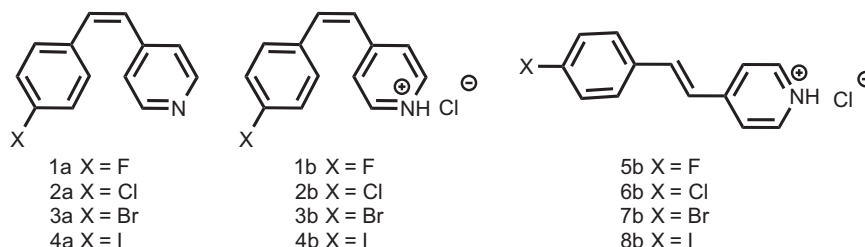
### 3. Experimental

#### 3.1. Synthesis of *cis*-stilbazole derivatives

The *cis*-stilbazoles were prepared by irradiation of the *trans* compounds in a  $\text{CHCl}_3$  solution in Pyrex test tubes ( $\lambda \geq 290$  nm), to afford a mixture of *cis* and *trans* and preparative TLC used to separate the liquid *cis* compound. The purity of *cis* compound was verified by  $^1\text{H}$  NMR and UV–vis spectrum (Fig. 1). The *cis* stilbazole. HCl salt formed on addition of 3 equivalents HCl (37%) was air dried overnight to give powder. These salts were vacuum dried for 12 h prior to irradiation.

#### 3.2. Irradiation technique

About 8–10 mg of stilbazole. HCl salts were spread uniformly between two Pyrex glass plates, sealed with parafilm and irradiated. The plates were turned around every 1 h, the samples thoroughly mixed and spread on the glass plate and irradiation continued. Irradiations were performed using a 450 W medium pressure mercury arc lamp placed in a water-cooled Pyrex immersion jacket. The progress of the reaction was monitored up to a maximum of 30 h. After a given duration of irradiation, a small portion of the irradiated solid material was dissolved in  $\text{H}_2\text{O}$  and neutralized with 1N NaOH. This neutral solution was extracted



**Scheme 2.** Structures of *cis* and *trans*-stilbazoles and their HCl salts discussed in this manuscript.

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