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Role of Hydrogen Bonds in Molecular Packing of Photoreactive Crystals: Templating Photodimerization of Protonated Stilbazoles in Crystalline State with a Combination of Water Molecules and Chloride Ions

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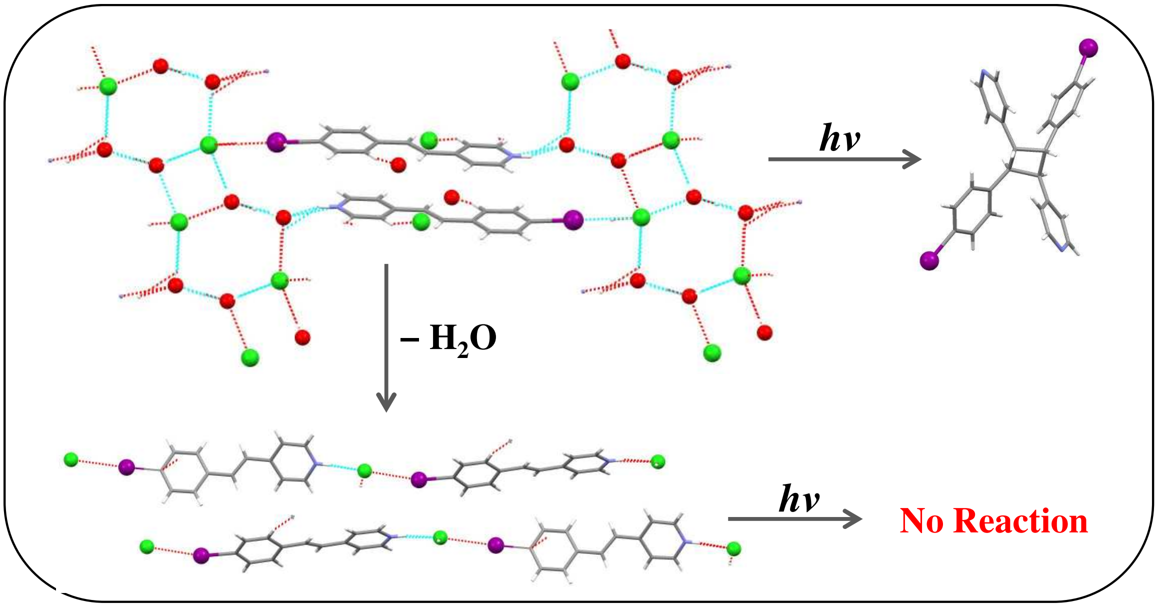
Abstract

A difference in photobehavior and molecular packing between hydrated and anhydrous crystals of protonated *trans*-stilbazoles has been identified. While stilbazoles are not photoreactive in the crystalline state, upon protonation with HCl in the solid state they dimerized to a single dimer (*anti-head-tail*) upon exposure to UV light. In these photoreactive crystals the protonated stilbazole molecules are arranged in a ladder-like format with the rungs made up of water molecules and chloride ions. A combination of water and chloride ion holds the protonated *trans*-stilbazoles through either N-H - - - O or N-H - - - Cl^- interactions. Anhydrous protonated stilbazole crystals prepared by heating the 'wet' crystals under reduced pressure were inert upon exposure to UV light. As per X-ray crystal structure analyses these lightstable crystals did not contain water molecules in their lattice. The current investigation has established that water molecules are essential for photodimerization of crystalline protonated *trans*-stilbazoles. To compare the reactivity of protonated *trans*-stilbazoles with that of protonated *cis*-stilbazoles, photoreactivity and packing arrangement of *cis*-4-iodo stilbazole. HCl salt were examined. This molecule in the crystalline state only isomerized to the *trans* isomer and did not dimerize. Thus, while the *trans* isomer dimerized and did not isomerize, the *cis* isomer only isomerized and did not dimerize in the crystalline state. To probe the role of cation---π interaction in the packing of protonated *trans*-stilbazoles, energies of various types of packing in the gas phase were estimated by MP-2 calculations and cation---π interaction was found to be unimportant in the packing of protonated *trans*-stilbazole crystals investigated here.

TOC



A combination of water molecules and chloride ions pre-orient protonated stilbazole molecules towards photodimerization the solid state.

Introduction

The first report of supramolecular photochemistry[1] whose history dates back to the late 1800s is probably the photodimerization of cinnamic acid derivatives in solid sate reported by Libermann in 1871.[2] The immense interest in solid state photochemistry evident from reports between 1900 and 1930 waned due to the lack of experimental techniques to uncover mechanisms of such reactions.[3, 4] Schmidt and co-workers' systematic study combining X-ray crystallography and photoreactions in the 1960s reignited this interest.[5] The term 'topochemical postulate' originally used by Kohlschutter in 1911 and Hertel in 1931 reworded by Schmidt as '*reaction in the solid state occurs with a minimum amount of atomic or molecular movement*' which is now known as 'Schmidt's topochemical postulate' forms the basis of organic solid state photochemistry.[6] According to the original topochemical postulate, photodimerization in the solid state is likely to occur when the separation between the reacting double bonds is less than 4.2 Å, are parallel, and one above other.[3] Several identified exceptions since the work of Schmidt have led to the conclusion that less than ideal atomic and orbital orientations can still lead to dimerization if the surrounding lattice can tolerate motions that would steer the molecules to proper mutual orientation, *i.e.*, some amount of tolerance in terms of distance (4.2 Å) and parallel arrangement of C=C bonds.[7] One of the major problems encountered in the current efforts devoted to establishing reliable strategies that would steer organic molecules toward a predetermined form is the lack of complete understanding of the intra- and intermolecular interactions that would lead to the observed crystal packing.[8-12] With this knowledge designing template groups, perhaps temporarily attached to the functional molecules to guide photochemically reactive groups into appropriate juxtaposition in crystals, would be feasible.

Three of the several distinct strategies that have been employed to bring the reactive molecules into proper orientations have yielded promising results:[4, 13-17] (a) Intramolecular substitution, (b) Templation with host structures and (c) Steering crystallization with a ditopic molecule capable of hydrogen bonding. In this regard chloro and fluoro substituents as steering groups and well-defined host systems such as inorganic hosts (zeolites and clays) and organic hosts (bis-urea and cucurbituril) to template photodimerization in the solid state have been exploited. The more popular approach of direct relevance to the current presentation is the ‘templation' strategy. Pioneering reports on this topic came from the group of Toda who used various 1,n-diols to orient olefins through weak intermolecular hydrogen bonds.[18-21] Scheffer, Ito and their co-workers exploited the stronger Coulombic acid-base interaction between the template amine and the reactant acid.[22, 23] MacGillivray and co-workers’ report on the templating strategy[24, 25] garnered the attention of a number of groups and restored interest to the area of solid state photodimerization.[26-28] They identified 1,3-dihydroxybenzene as a template to pre-orient 4,4’-bispyridylethylene (4,4’-BPE) towards dimerization in the crystalline state. Along this line we recently demonstrated the value of thiourea as a template to pre-orient eleven stilbazoles and azastilbenes in the crystalline state toward a single dimer product.[29] Despite the established utility of thiourea and 1,3-dihydroxybenzene as templates, no single universal template that would steer ‘majority’ of molecules toward a dimer has been identified. Search for templates and understanding their function therefore continue unabated in organic solid state photochemistry.

In this article we present our results on the solid state photodimerization of stilbazoles. Like cinnamic acids, stilbazoles have played historically an important role in photodimerization. When Schmidt was exploring the dimerization of cinnamic acids at the Weizmann Institute,[5] Williams of Kodak Research Laboratories, concurrently irradiating several protonated stilbazoles in the solid state noted differences in reactivity between solution and solid state, and between various substituted derivatives in the solid state.[30-32] It is interesting to note that while the former explored from a ‘basic science’ perspective, Williams did it for lithographic applications.[33] Photodimerization of protonated stilbazoles has since been investigated in monolayer assemblies, micelles, membranes and within various host structures such as cyclodextrins, calixarenes and cucurbiturils.[34-42] We recently communicated in this journal that HCl salts of numerous stilbazoles dimerized readily in the crystalline state while neutral stilbazoles were inert.[43] Although the packing arrangements of seven reactive and two non-reactive stilbazoles were presented, with the respective CIF files deposited with CCDC, we did not elaborate on the forces that may be involved in the packing of protonated stilbazoles and did not correlate reactivity with packing. Following our brief communication, we have carefully examined the packing arrangements and photochemistry of the reactive, non-reactive and dry (water-free) protonated stilbazoles and the results are presented in this article. In addition, since the stilbazole is protonated and carries a positive charge we were curious to examine the role of cation-π interaction on crystal packing.[44, 45] In this context, we have examined the location of the positive charge in the protonated stilbazole molecule by computation and estimated the energies of the various arrangements for a pair of protonated stilbazoles. The results of these studies are presented and discussed below.

Experimental

Synthesis and sample characterization: *trans*-Stilbazole derivatives were synthesized following literature procedures.[46-48] The corresponding HCl salts were prepared by adding 2 equivalents of conc. HCl to stilbazoles in a mortar and grinding with a pestle to give a paste. The HCl salt whose formation was inferred from the color change in stilbazoles upon addition of conc. HCl was air dried overnight to give a powder of *trans*-stilbazole.HCl salt. These powders with 10 – 20 % water as determined from thermogravimetric analysis (TGA) using Netzsch Thermal Analyzer were considered to be hydrated salts. The TGA data are provided in Table 1. The anhydrous stilbazole.HCl salts obtained by drying the hydrated salts at ~110 °C under reduced pressure (10^{-2} torr), for 7-9 h were stored in vials in a desiccator. The anhydrous nature was confirmed by recording the weight loss by TGA measurements. For TGA experiments 2-4 mg of powder sample was used and the temperature range was set between 25-120° C with a heating ramp of 5° /min to confirm.

Photoreaction and product characterization: Irradiations were performed using a 450 W medium pressure mercury arc lamp kept in a water-cooled Pyrex immersion well (transmission $\lambda \geq 290$ nm). Hydrated and anhydrous crystals were irradiated by uniformly spreading 8-10 mg of salt between two Pyrex plates sealed with parafilm and by turning the plates around every 1 h for uniform exposure. After irradiation the powder was dissolved in water and neutralized with 1N NaOH, extracted four times with chloroform and the combined organic layer dried over anhydrous Na_2SO_4. Product was obtained upon solvent evaporation and was characterized by ^1H NMR in $CDCl_3$. ^1H NMR spectra of the dimers are available in the ESI of our earlier communication. The isomer was confirmed by solving the structure by X-ray crystallography.

Table 1 Water content in the crystal before irradiation[a]

Sample	% H_2O loss from TGA experiment	% H_2O present in crystal structure
1.HCl.3H_2O	19.3	19
2.HCl. 3H_2O	13.6	19
3.HCl. 2H_2O	11	12
4.HCl. 2H_2O	7.8	10
5.HCl. 2H_2O	6.8	9
7.HCl. 8/3H_2O	9.8	15
8.HCl. 3H_2O	13.1	17[b]

[a] Microcrystalline powder for TGA measurements and single crystal for crystal structure analysis single were used.
[b]Data taken from ref. 43.

Crystallographic Analyses: Details regarding the hydrated crystals were presented in our previous communication and will not be repeated here. This article reports crystal structures of three anhydrous *trans* isomers and a *cis* isomer of protonated substituted stilbazoles. Yellow single crystals of anhydrous **3**.HCl and **4**.HCl, suitable for X-ray diffraction analyses were obtained by evaporation of solvent from an anhydrous methanol solution at 25 °C in a glove box. Yellow single crystals of anhydrous **5**.HCl suitable for X-ray diffraction analyses were obtained by evaporation of solvent from an anhydrous ethanol solution at 25 °C in a glove box. Light yellow single crystals of **11**.HCl suitable for X-ray diffraction analyses were obtained by evaporation of solvent of a mixture of ethyl acetate/chloroform solution at 25 °C. Each data crystal was glued onto the end of a thin glass fiber. X-ray intensity data were measured by using a Bruker SMART APEX2 CCD-based diffractometer using Mo Kα radiation (λ = 0.71073 Å).[49] The raw data frames were integrated with the SAINT+ program by using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied with SAINT+. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied using the program SADABS. All structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares on F^2, by using the SHELXTL software package.[50, 51] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as standard riding atoms during the least-squares refinements. Crystal data, data collection parameters, and the results of the analyses are listed in Table 2.

Compounds **3**.HCl and **4**.HCl crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with either of the space groups $P2_1$ or $P2_1/m$. The latter was chosen and confirmed by the successful refinement and solution of the structure. With Z = 2, both molecules have crystallographic mirror symmetry. The alkene group of the cationic stilbazole molecule in both complexes is disordered over two orientations, which were refined in a 50:50 ratio. One molecule of methanol cocrystallized with the complex and was included in the analysis. Compound **5**.HCl crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful refinement and solution of the structure. The asymmetric crystal unit contains two molecules of **5**.HCl. Compound **11**.HCl crystallized in the monoclinic crystal system. The systematic absences in the intensity data were consistent with the unique space groups $P2_1/c$.

Computational Details: All calculations were performed using the Gaussian 09 program.[52] The geometry of stilbazole.H^+ monomer was optimized at the B3LYP/6-311+G(d,p) level.[53-55] To study the interactions between two stilbazole.H^+ molecules, four different arrangements (a, b c, and d in Figure 12) were optimized at the second-order Møller-Plesset (MP2) level of theory using the 6-31G(d) basis set.[56-58] All aforementioned structures were optimized in the gas phase without any symmetry constraints.

Table 2. Crystallographic Data for Protonated Stilbazoles **3**, **4**, **5** and **11**.

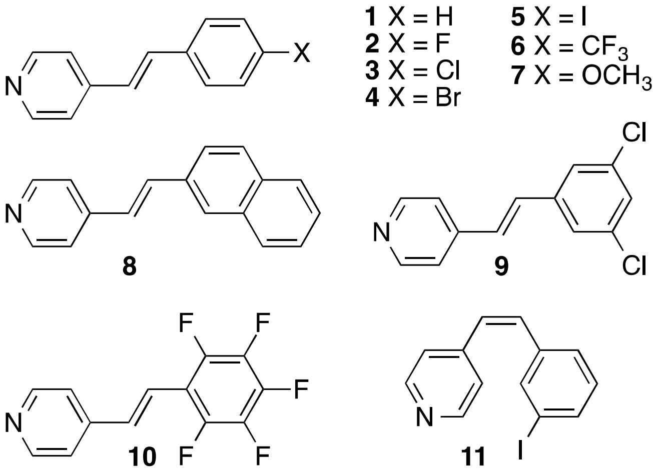
	3.HCl	**4.HCl**	**5.HCl**	**11.HCl**
Empirical formula	$C_{13}H_{11}NCl{\bullet}Cl\ CH_3OH$	$C_{13}H_{11}NBr{\bullet}Cl\ CH_3OH$	$C_{13}H_{11}NI{\bullet}Cl$	$C_{13}H_{11}NI{\bullet}Cl$
Formula weight	284.17	328.63	343.58	343.58
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Lattice parameters				
a (Å)	4.7953(5)	4.8200(5)	8.6445(5)	14.0901(6)
b (Å)	8.5668(8)	8.7182(9)	12.0822(6)	8.0051(3)
c (Å)	17.3529(18)	17.3278(17)	13.2869(7)	12.3594(5)
α (deg)	90	90	103.255(1)	90
β (deg)	90.321(2)	90.278(2)	107.303(1)	107.537(1)
γ (deg)	90	90	97.032(1)	90
V (Å^3)	713.15(12)	728.14(13)	1262.22(12)	1329.26(9)
Space group	$P2_1/m$ (# 11)	$P2_1/m$ (# 11)	$P\ \bar{1}$ (# 2)	$P2_1/c$ (# 14)
Z value	2	2	4	4
ρ_{calc} (g / cm^3)	1.323	1.499	1.808	1.717
μ (Mo Kα) (mm^{-1})	0.443	2.994	2.720	2.583
Temperature (K)	296	296	296	296
$2\Theta_{max}$ (°)	50.00	53.98	56.00	57.98
No. Obs. (I > 2σ(I))	1090	1270	5290	3064
No. Parameters	109	109	289	145
Goodness of fit	1.054	1.025	1.035	1.015
Max. shift in cycle	0.000	0.002	0.002	0.003
Residuals*:R1; wR2	0.0379; 0.0988	0.0370; 0.0841	0.0272; 0.0654	0.0262; 0.0662
Absorption Correction, Max/min	Multi-scan 0.9825/0.8291	Multi-scan 0.7457/0.5597	Multi-scan 0.8538/0.4764	Multi-scan 0.7461/0.6207
Largest peak in Final Diff. Map (e$^-$ / Å^3)	0.290	0.469	0.606	1.019

*$R = \Sigma_{hkl}(\,||F_{obs}| - |F_{calc}||\,)/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}{}^2]^{1/2}$,
$w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/(n_{data} - n_{vari})]^{1/2}$.

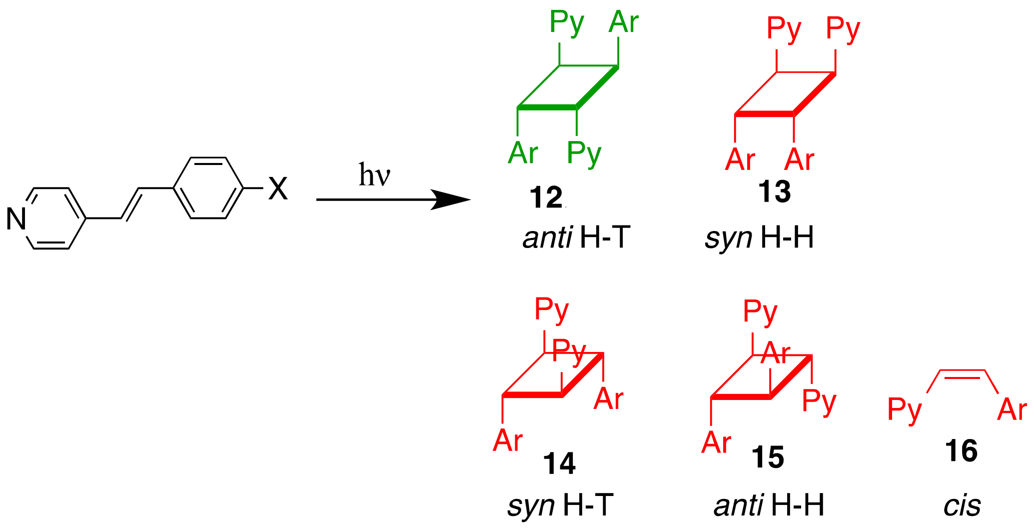
Results and Discussion

In this article we focus our discussion on ten (**1-10**; Scheme 1) of the sixteen protonated *trans*-stilbazoles whose reactivity and X-ray structures we had previously reported in a communication.[43] Eight (**1-8**) of the ten (**1-10**) stilbazole.HCl salts upon irradiation in the crystalline state dimerized to a single dimer product (*anti-head-tail;* Scheme 2). The ^{1}H NMR spectral pattern was consistent with that of *anti-head-tail* dimer whose structure was confirmed by single crystal X-ray diffraction analysis for the dimer from stilbazole (Figure 1). Since ^{1}H NMR spectra of the dimers are available in the ESI of our earlier communication[43] they are not reproduced here. The packing arrangements of eight reactive (**1-8**) (structure for **8** was taken from the literature[44]) and two non-reactive (**9** and **10**) stilbazole.HCl salts are presented in Figures 2-5. It is clear from these figures that the reactive ones contain water in their lattice (Figures 2-4) while the two unreactive stilbazole salts do not contain water molecules (Figure 5) suggesting the possible role of water for their reactivity.

To examine the role of water in the above reactive crystals, seven reactive stilbazole.HCl salts (**1-5**, **7** and **8**) were crystallized under dry conditions and examined for reactivity by irradiation (for the same time periods by which time the hydrated crystals dimerized). They were found to be inert. The progress of the reaction of the dry and wet crystals of 4-iodostilbazole, an example, is presented in Figure 6. Examination of Figures 6 a-c indicates that while the wet sample has dimerized to about 49%,(with 5h of irradiation) the dry sample has not reacted. Similar results were observed with other samples as well. Quantitative conversion to dimer was achieved in about 15 h in all cases. For comparative (dry and wet samples) studies the solids were irradiated for a shorter time to prevent the dry samples from absorbing posture from the humid laboratory. Furthermore, inclusion of water in the wet crystals and the lack of it in the dry crystals in the solid state were confirmed by estimating the water content by TGA (Table 1). The water content as measured by thermogravimetry and estimated from crystal unit cell are close and in the range of 10-20%. The difference in water content in some cases between TGA measurements and that estimated from X-ray crystal structures is possibly due to the nature of samples used for these two studies; powder for TGA and single crystals for X-ray data collection. To shed more light on the lack of reactivity of anhydrous crystals attempts were made to obtain single crystals of dry **1**-**7** HCl salts. However, only three anhydrous samples (**3**-**5**) gave single crystals suitable for X-ray analysis and the packing arrangements for them as obtained from X-ray structure determination are presented in Figures 7 and 8. As evident from the figures two of these crystals contained methanol from the crystallization solvent instead of water in the lattice.



Scheme 1 Structures of stilbazoles investigated. All stilbazoles were protonated with HCl before irradiation.



Scheme 2. Compound **12** (shown in green) is obtained while the other possible products **13-16** (shown in red) are not obtained from irradiation of hydrated crystals of **1-10**. In the product structures H = head; T = tail.

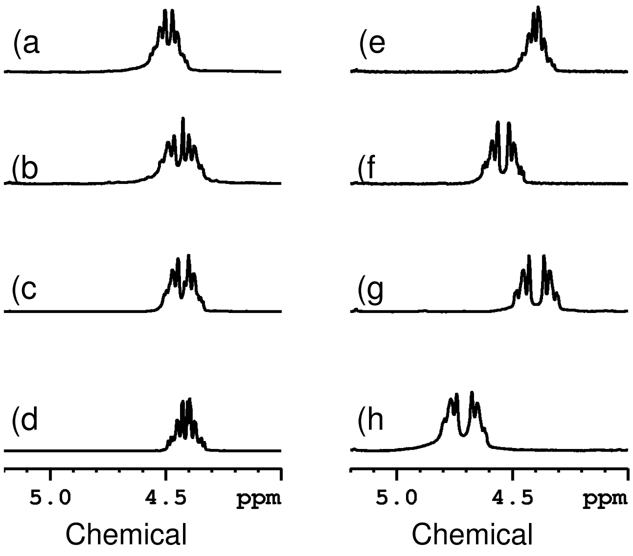


Figure 1 ^{1}H NMR ($CDCl_3$) signals of cyclobutane protons in the dimers obtained from **1-8**.HCl xH_2O. Dimers from irradiation of **1-8**.HCl xH_2O are shown in order (a)-(h) respectively.

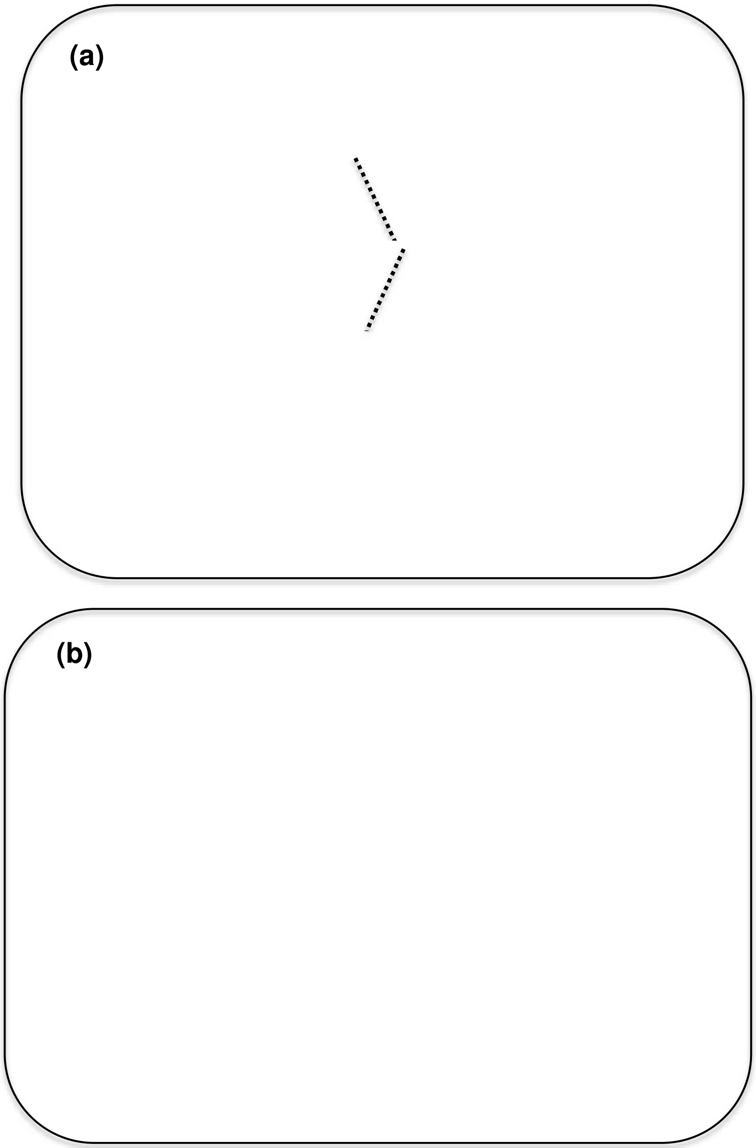


Figure 2 (a) **1**.HCl. $3H_2O$ (b) **8**.HCl. $3H_2O$. Oxygen of H_2O represented as red sphere and Cl^- as green sphere. Data for (b) taken from ref. 44.

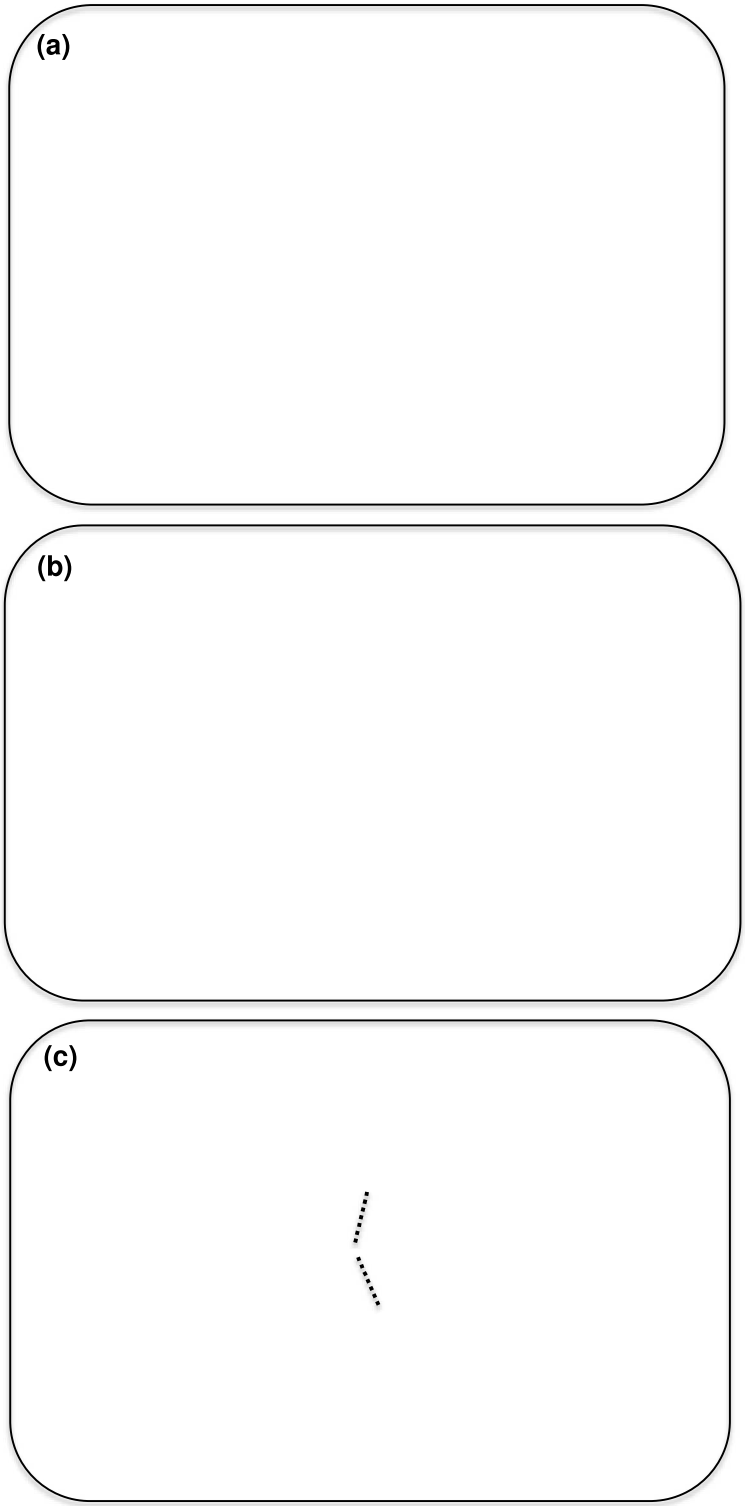


Figure 3 (a) **4**.HCl. $3H_2O$ (b) **5**.HCl. $2H_2O$ (c) **6**.HCl. $3H_2O$. Oxygen of H_2O represented as red sphere and Cl^- as green sphere.

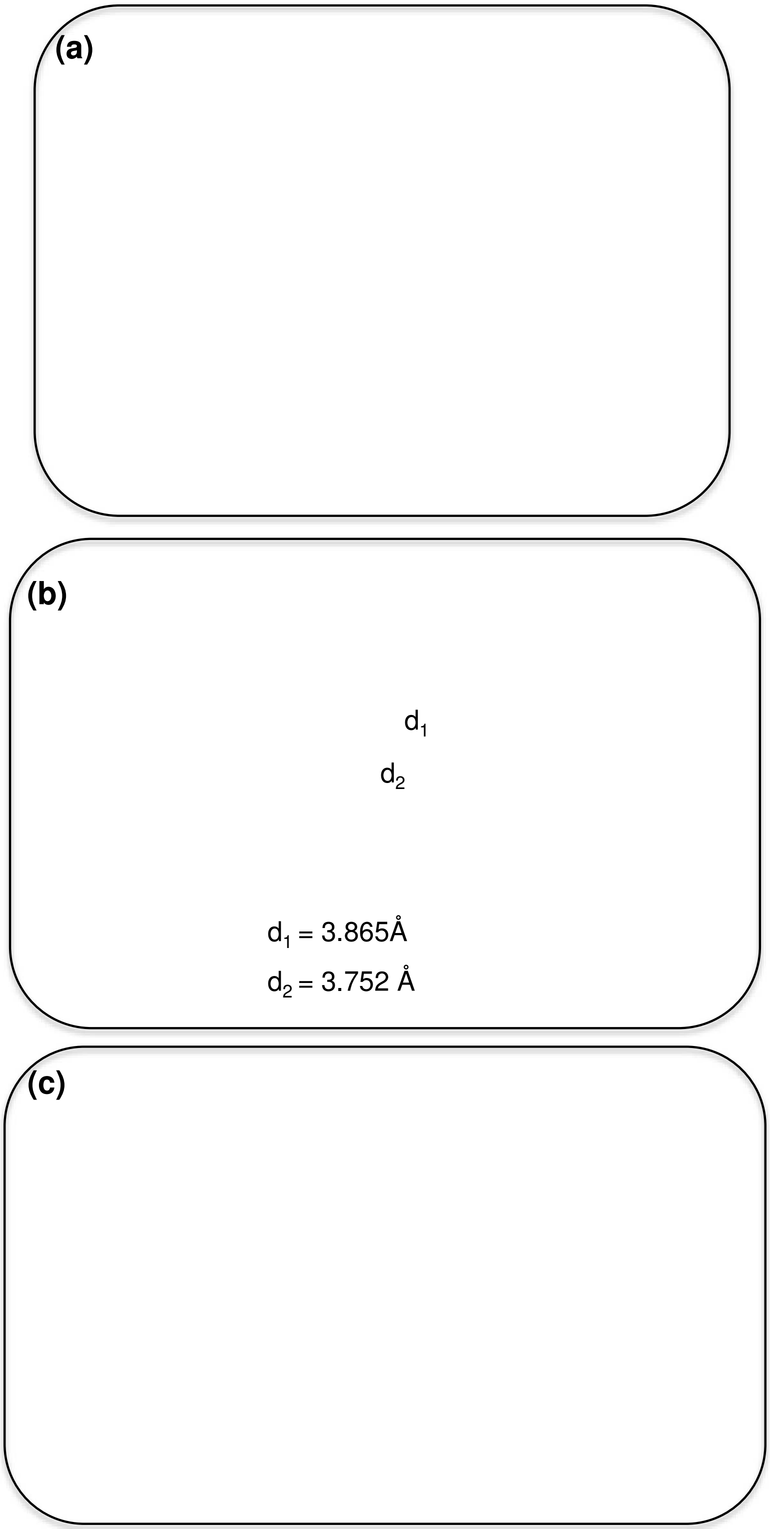


Figure 4 (a) **2**.HCl. 3H_2O (b) **3**.HCl. 2H_2O (c) **7**.HCl. 8H_2O. Oxygen of H_2O and -OCH_3 represented as red sphere and Cl^- as green sphere.

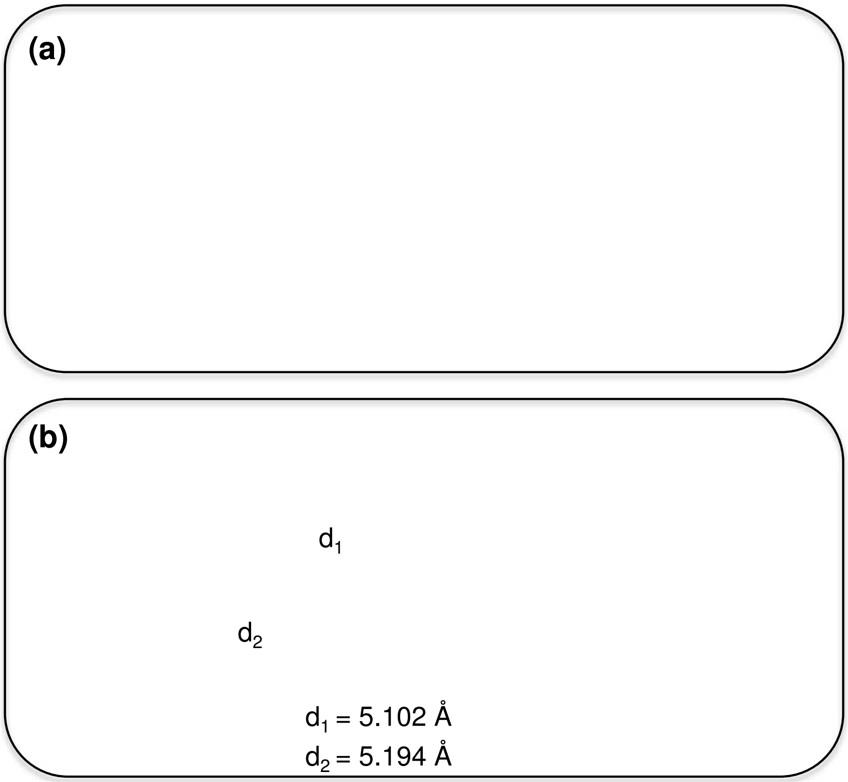


Figure 5. Non-reactive derivatives (a) **9**.HCl (b) **10**.HCl. Cl^- is represented as green sphere.

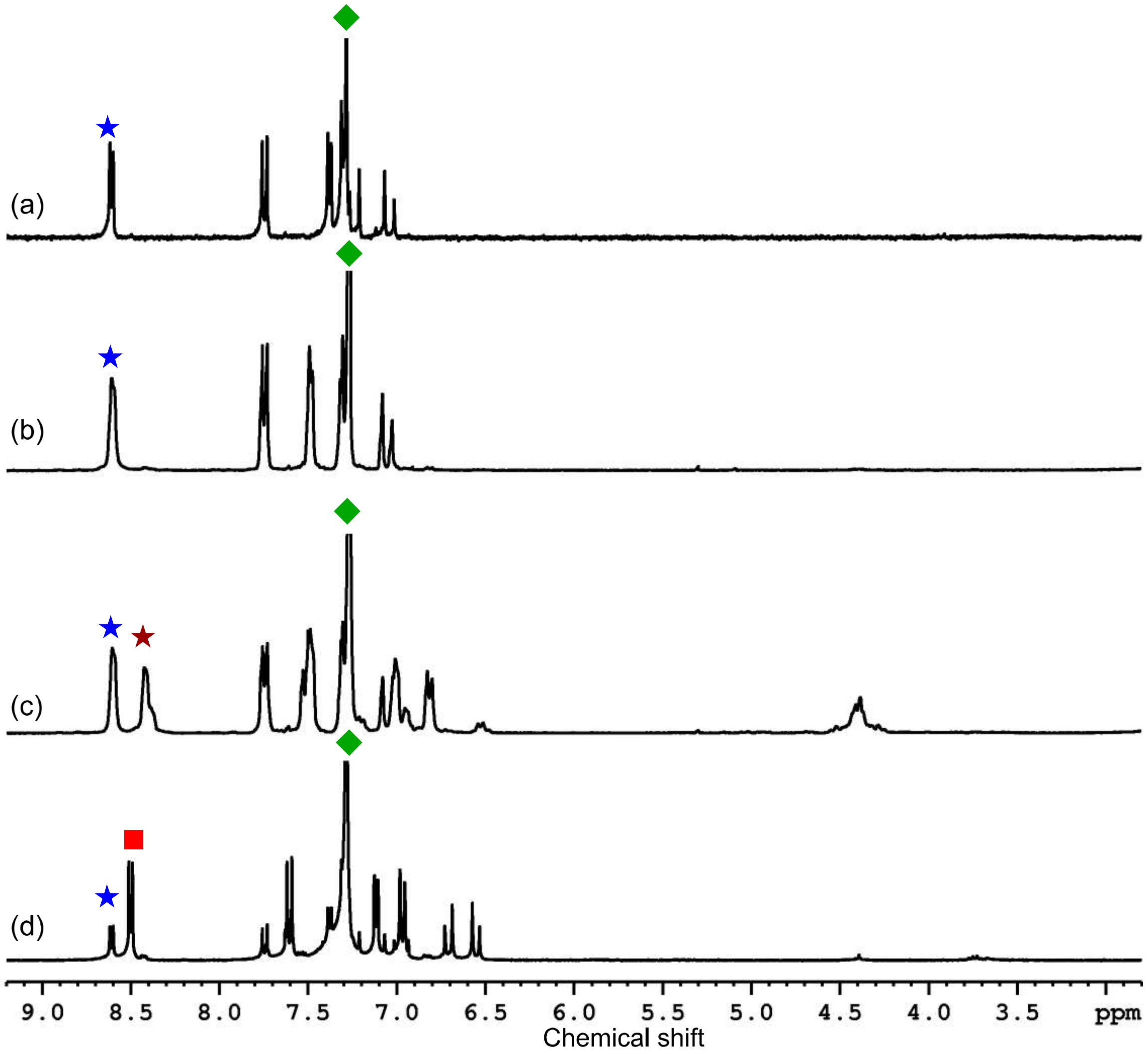


Figure 6 (a) ^{1}H NMR (300 MHz) in $CDCl_3$ of **5** (b) neutral extract of anhydrous **5**.HCl, irradiated for 5 h in solid state, (c) neutral extract of **5**.HCl.2H_2O, irradiated for 5 h in solid state. (d) neutral extract of 11.HCl, irradiated for 5 h in solid state. The anhydrous **5**.HCl shows no dimer formation, while the hydrous salts shows 49% conversion to dimer and the **11**.HCl shows 11% conversion to *trans*. Aromatic proton *ortho* to N in pyridyl ring is denoted by '▯' for *trans*, '■' for *cis* and '▯' for *anti* H-T dimer. Solvent residual peak of chloroform is denoted by '◆'.

(a)

(b)

Figure 7 Anhydrous structures (a) **3**.HCl.MeOH (b) **4**.HCl. MeOH. Oxygen of methanol represented as red sphere and Cl^{-} as green sphere.

(a)

(b)

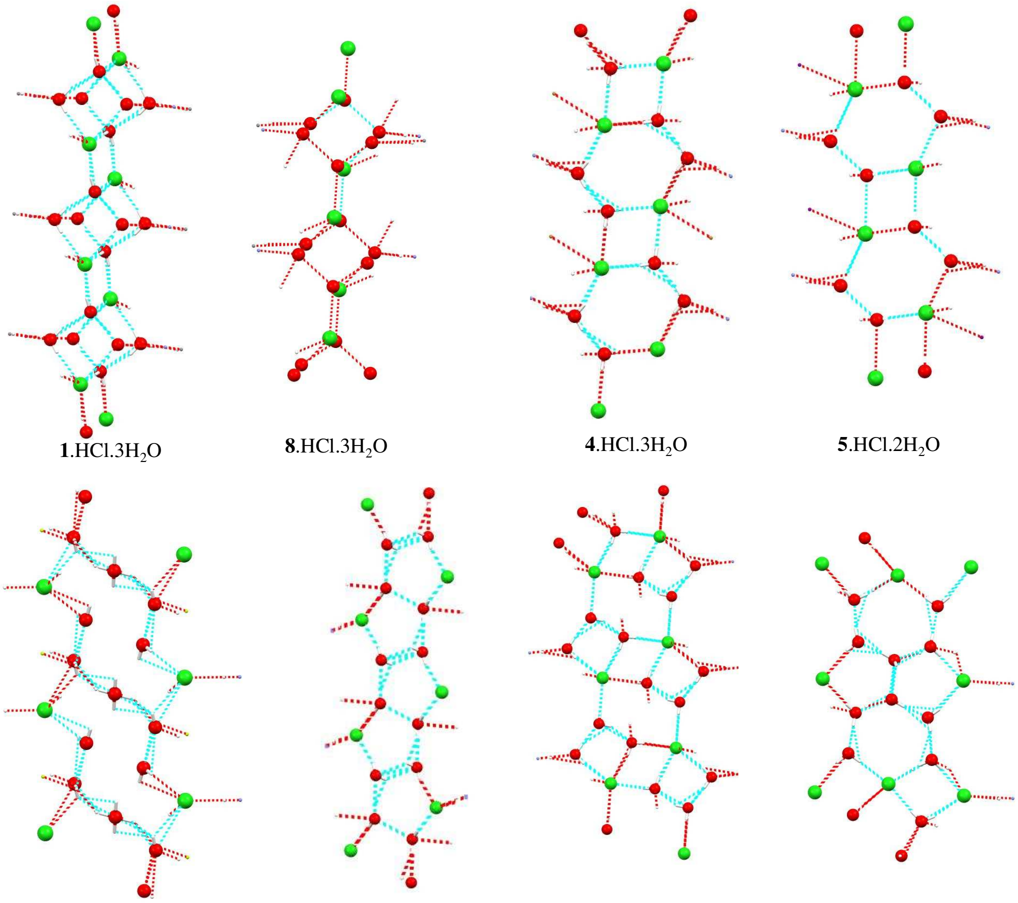
Figure 8 Anhydrous structures (a) **5**.HCl (b) **6**.HCl. Cl^{-} is represented as green sphere. Data for (b) taken from ref. 45.

First we discuss the packing arrangements of the photoreactive stilbazole.HCl salts (**1**-**8**) with water molecules in their lattice. Examination of Figures 2-4 leads to the following conclusions: (a) Adjacent pairs of stilbazole molecules are within 4.2 Å and parallel to one another. (b) The two olefins are arranged in a head to tail centrosymmetric fashion with respect to one another, (*i.e.*, α-packing as per Schmidt's cinnamic acid nomenclature[59]). (c) The pairs of molecules as arranged above upon excitation could smoothly transform to *anti-head-tail* dimer (consistent with the photochemical results mentioned in the previous paragraph). (d) Although the elegant ladder-like stacking of stilbazole molecules in the lattice seem similar between the diagrams, the side rails holding the rungs of the ladder differ significantly between the eight reactive molecules. This observation is quite different from the thiourea template we reported earlier[29] where the rungs and side rails looked closely similar for the ten different stilbazoles. (e) As illustrated in Figure 9 there are six different arrangements for the side rails made up of water molecules and chloride ions for the eight protonated stilbazoles. (f) In all cases the ladder-like packing of the reactive protonated stilbazoles are held by the rungs made up of water molecules or chloride ions. A combination of water and chloride ion holds the stilbazole-H^+ through either N-H - - - O or N-H - - - Cl^- interactions. Of the eight packing arrangements five are held by N-H - - - O bonding (Figures 2 and 3)[60, 61] and the remaining by N-H - - - Cl^- (Figure 4). (g) The hydrogen bonding between the three, pyridinium N—H, water and chloride ions are interdependent for the stability and arrangement of the lattice.

Figures 2-4 reveal that in each case the olefin in the middle could react with the one above or below (the three olefins are indicated with distances between them) to give the same product *anti-head-tail* dimer. The distances between the two possible reactive pairs are provided in these figures. In all cases except Figures 3 (a) and (b) the distance between the two pairs are close and less than 4.2 Å. In principle any one of the two pairs could initiate the dimerization. In the case of **4**.HCl. 3H_2O and **5**.HCl. 2H_2O (Figures 3 (a) and (b)) one pair is within 4.2 Å and the other pair is separated by more than 4.2 Å. It is likely that the pair with a distance of less than 4.2 Å reacts to yield the *anti-head-tail* dimer. Regardless of the specificity of the reacting pair quantitative conversion would be expected in all cases.

The above eight protonated stilbazoles, all containing water in their crystal lattice photodimerized to a single *anti-head-tail* dimer product within 5 h upon irradiation with 450 W medium pressure lamp through a Pyrex glass plate. For total conversion a much longer time was required. As illustrated in Figure 5, the protonated stilbazoles **9** and **10** which are unreactive in the crystalline form do not contain water in the lattice and the adjacent molecules are separated by > 4.9 Å. One should note that in reactive crystals the reactive molecules were separated by less than 4 Å. This difference between the two sets highlights the importance of water in packing molecules in a topochemically favorable arrangement. Our attempts at crystallizing stilbazole.HCl **9** and **10** with water (in their lattices), to test if the presence of water would make them reactive, were not successful. We therefore decided to crystallize the reactive protonated stilbazoles **1**-**8** without water and examine their reactivity and packing. As mentioned above, seven (**1-5**, **7** and **8**) of the eight protonotated stilbazoles were obtained as powders (without water) and upon excitation remained unreactive. Of the seven inert protonated stilbazoles four gave single crystals (**3**-**6)** suitable for X-ray diffraction studies. Their crystal packing shown in

Figures 7 and 8 account for their inertness. In all cases the adjacent olefins are > 4.7 Å apart and the olefinic π-bonds are slipped with respect to each other. From the above experiments it is clear that water molecules play a critical role in templating the protonated stilbazoles toward photodimerization in crystals. We were unable to test whether Cl^- is essential or any other anion would function as a template along with water molecules. When HBr, HI and $HClO_4$ were used to protonate the stilbazole a wet paste was obtained that could not be dried to a powder suitable for irradiation. Therefore at this stage we assume that Cl^- in combination with water is a useful template for protonated stilbazole. We plan to pursue experiments to probe whether Cl^- is unique or whether any other anion in combination with H_2O would be able to template the olefins.



1.$HCl.3H_2O$ **8**.$HCl.3H_2O$ **4**.$HCl.3H_2O$ **5**.$HCl.2H_2O$

2.$HCl.3H_2O$ **3**.$HCl.2H_2O$ **6**.$HCl.3H_2O$ **7**.$HCl.8H_2O$

Figure 9 H_2O and Cl^- motifs formed. Oxygen of H_2O represented as red sphere and Cl^- as green sphere.

Examination of the packing arrangements shown in Figures 2-4 reveals that the hydrogen bonding between N—H --- O and N—H - - - Cl^{-} control the packing. In addition hydrogen bonding between Cl^{-} and H_2O is essential for building a running template along both the sides of the reactive olefins. As evident from the Figures 5, 7 and 8, without water, Cl^{-} alone cannot build a rail to hold the rungs of the ladder. The above studies have established that templation of the protonated stilbazoles could be brought about with a composite of water and chloride ion. Both are essential for the photodimerization of protonated stilbazoles in the solid state.

Two common known photoreactions of olefins in solution are unimolecular geometric isomerization and bimolecular dimerization.[62] In solution the geometric isomerization competes effectively with the diffusion controlled dimerization process. On the other hand, in crystals the need for diffusion of the two molecules towards one another if eliminated through pre-organization, the dimerization is the main reaction. In addition, generally the geometric isomerization requiring considerable free space around the excited molecule does not occur in close packed crystals. Because of the horizontal planar structure, *trans*-olefins tend to pack tightly as compared to slightly twisted *cis*-olefins. This reduces the probability of *trans* to *cis* isomerization in crystals[63, 64] while several examples of *cis* to *trans* isomerization of olefins in crystals are known.[65-68] However, the mechanism of geometric isomerization in crystals is less well established than in solution.

Following the success with the photodimerization, we decided to examine the geometric isomerization of *trans* and *cis*-stilbazole.HCl salts as crystals. None of the hydrated or anhydrous *trans*-stilbazole.HCl salts upon excitation isomerized to the *cis*-isomer; they either dimerized or were inert. This is consistent with the known behavior of *trans*-cinnamic acids. On the other hand, exposure of several *cis*-stilbazole.HCl salts to light resulted in conversion to the *trans* isomer. In this article, we present results on one system namely, *cis*-4-iodo stilbazole. HCl salt (**11**; Scheme 1). Crystallization of *cis* 4-iodo stilbazole. HCl salt in a manner similar to the *trans* isomer under normal laboratory conditions, surprisingly gave crystals without inclusion of water molecules. Note that under such conditions the *trans* isomer crystals included water molecules (Figure 3b). *Trans* 4-iodo stilbazole.HCl salt could also be crystallized without water as shown in Figure 8a. Thus, these three crystals presented an opportunity to compare the packing and photoreactivity of *trans* 4-iodo stilbazole.HCl salt under hydrated and anhydrous conditions and the *cis* 4-iodo stilbazole.HCl salt under anhydrous conditions. The packing arrangement of *cis* 4-iodo stilbazole.HCl salt is presented in Figure 10. The packing is facilitated by N–H---Cl$^-$ and π–––π interactions (see Figure 10a); interestingly the protonated pyridyl rings are arranged parallel in a head-tail fashion within 3.97 Å. Probably π–––π interaction favors stacking of the two rings, and electron deficiency of the pyridyl ring due to protonation prompts head-tail arrangement. Also noteworthy is that since the adjacent C=C bonds are far apart (> 8 Å; Figure 10b),dimerization is not expected. Such loose packing of these crystals as compared to the *trans* 4-iodo stilbazole.HCl (anhydrous and hydrated; Figures 3b and 8a) is likely to favor geometric isomerization upon excitation. As expected, irradiation of *cis* 4-iodo stilbazole.HCl crystals gave the corresponding *trans* isomer as the only product; no dimers were obtained. The ^{1}H NMR spectra of the three irradiated samples (hydrated and anhydrous *trans* 4-iodo stilbazole.HCl salts and anhydrous *cis* 4-iodo stilbazole.HCl salt) presented in Figure 6 clearly highlights the reactivity differences between the three crystals. The hydrated *trans* crystal dimerized to a single *anti-head-tail* dimer (**12** in Scheme 2; Figure 6c); the anhydrous *trans* crystals were photostable (Figure 6b) and the anhydrous *cis* crystals isomerized to the *trans* (Figure 6d). The photochemical behavior is consistent with the expectations based on crystal packing. It is important to note the crystal packings of both *trans* and *cis* 4-iodo stilbazole.HCl salts do not favor dimerization (Figures 8a and 10). Thus a geometric isomerization pathway is open to both molecules in the excited state. However, only the *cis* isomer isomerizes to *trans*, but the *trans* isomer does not react. This suggests that careful analysis of the packing is required to understand the difference. We are currently carrying out experiments to probe the mechanism of geometric isomerization of olefins in crystals.

(a)

(b)

Figure 10 Partial packing arrangement of **11**.HCl. (a) Distance between the two planes defined by the two pyridinium rings is 3.397 Å. Cl^{-} is represented as green sphere. (b) Distance between the C=C bonds is 8.005 Å. Cl^{-} are omitted for clarity.

In the literature cation-π interaction is suggested to be important in packing of protonated *trans*-stilbazole molecules in a photodimerizable arrangement.[44, 45, 69, 70] The fact that the crystals of **3-6** HCl not containing water molecules are not reactive suggested that cation-π interaction is less important than hydrogen bonding of N—H with water molecules and chloride ions. More importantly, we reasoned that in protonated stilbazoles the positive charge would be localized on the N—H σ-bond rather than on the π-cloud of the pyridyl ring. If this is true we believed that the two reactive olefins would be perpendicular to each other and would not be in the correct geometry for dimerization. To examine the location of the positive charge in the protonated stilbazole, we optimized its structure at the B3LYP/6-311+G(d,p) level and calculated the charges on all atoms. The charges on the optimized structure are shown in Figure 11. It is important to note that the carbon atoms carry the negative charge and all the hydrogens atoms are positively polarized. As intuitively predicted the hydrogen atom bound to the nitrogen atom (N—H) carries the largest positive charge (+0.43) and the negative charge (– 0.48) resides on the nitrogen atom. This clearly suggests that the protonated stilbazole is positively polarized along the N—H σ bond. To probe how this positively polarized N—H bond would interact with another protonated stilbazole we optimized four structures (Figure 12 a, b c, and d) at the second-order Møller-Plesset (MP2) level of theory using the 6-31G(d) basis set.[56-58] Structures and energies of the four structures are shown in Figure 12. Two structures (a and d) correspond to the N—H bond being oriented towards the π cloud of the two rings (cation-π interaction), pyridyl and phenyl and the other two structures correspond to the two olefin molecules being one on top of each other in a parallel fashion in head to tail (b) and head to head (c) fashion. Because the pyridyl part is electron deficient and the phenyl part is relatively electron rich the structure (b) could be more stable due to charge transfer interaction and the arrangement (d) would be least stable due to charge repulsion. Of the four structures shown in Figure 12 only the head-tail arrangement shown in Figure 12 (b) would give the observed dimer. According to MP2 calculations, of the four arrangements the most stable one in the gas phase is the structure shown in Figure 12 (a) in which the two olefins are nearly perpendicular to each other. The next most stable one is the head-tail arrangement shown in Figure 12 (b). In this case the stability (although lower than cation-π interaction) results from charge-transfer interaction between the electron deficient pyridyl and electron rich phenyl rings. The fact that this arrangement is preferred in crystals, according to crystal structure analysis (Figures 2-4), suggests that hydrogen bonds between stilbazole-H^+ and water molecules or chloride ions provide enough energy to overcome the cation-π interaction. Thus based on MP2 calculations we conclude that the packing in protonated stilbazoles are stabilized by hydrogen bonds and charge transfer interaction[43] rather than by cation-π interaction. The approach we have adopted also illustrates that the quantum chemical calculations could be a valuable tool in solid-state photochemistry to infer molecular packing in crystals. Combining crystallography, photochemistry, quantum chemistry and solid state techniques could be valuable in solving problems in solid state photochemistry that seems to be complex and challenging.

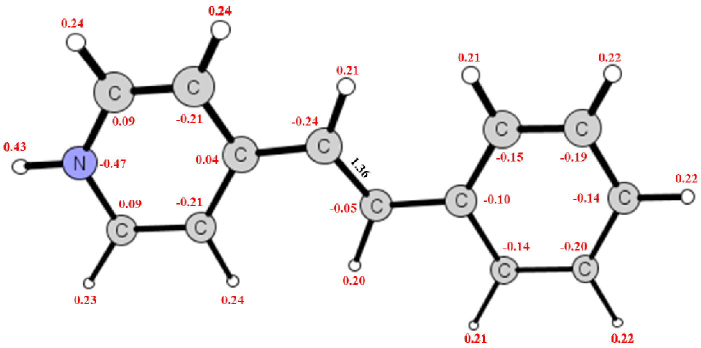
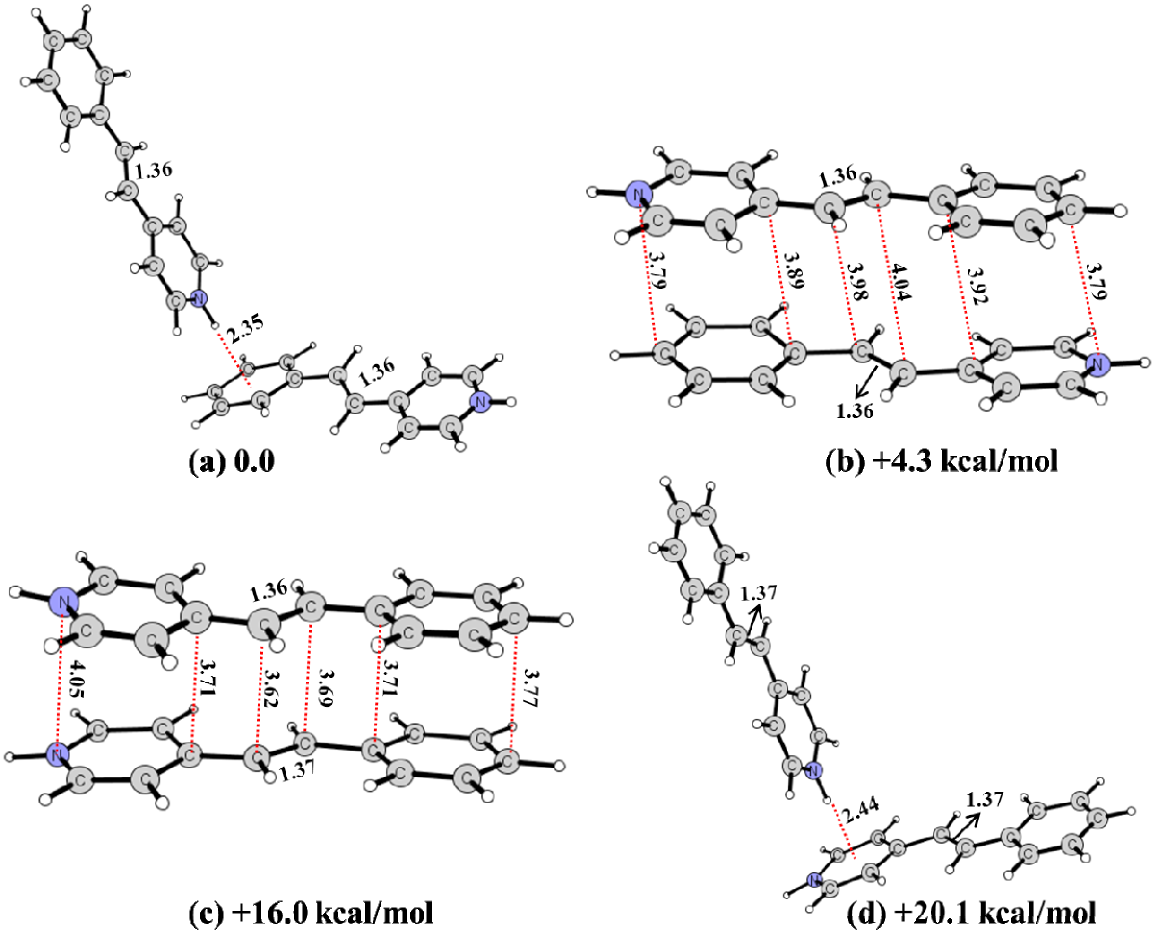


Figure 11 Charge distribution in the case of protonated *trans*-stilbazole as calculated by at the B3LYP/6-311+G(d,p) level



(a) 0.0

(b) +4.3 kcal/mol

(c) +16.0 kcal/mol

(d) +20.1 kcal/mol

Figure 12 Structures and energies of pairs of protonated *trans*-stilbazole molecules in the gas phase optimized at the second-order Møller-Plesset (MP2) level of theory using the 6-31G(d) basis set.

Conclusions

Photodimerization continues to play a key role in the development of the field of organic solid state photochemistry. The unfortunate unpredictability of solid-state photoreactions, with its history dating back to the late 1800, is intimately linked to crystal engineering which despite the considerable interest and development, is yet to become a predictable science. One of the current methods of organic solid-state photodimerization termed templated photodimerization involves the use of a template whose bonding properties with the reactant molecules are better understood than the intermolecular interactions between the reactants themselves. In this article we have identified a mixture of water and chloride ions that serve as a template to orient protonated stilbazoles toward photodimerization in the solid state. It is important to note that unlike thiourea, 1,3-dihydroxybenzene and other ditopic templates the system identified here is unlikely to serve as a universal template. The weak interactions identified here is specific to the olefins investigated here. However, two common molecules, water and chloride ion, together are able to template a number of protonated stilbazoles is interesting and calls for in further understanding of principles of crystal engineering.

By combining X-ray crystallography and photochemistry we have established that water molecule and chloride ion has the potential to be a general template (13 of the 16 protonated stilbazoles reacted; success rate 81%). The templation is facilitated by weak interaction between PyN^{+}—H and water or PyN^{+}—H and Cl^{-}. In spite of the reported success, it is not obvious which of the two interactions is going to be dominant in a given case and it is also not clear whether this approach would apply to other olefins as well. During the last decade several templates have been identified, each one with its own advantages and disadvantages, but they all suggest that further work is needed. The field of organic solid state photochemistry combined with crystal engineering has plenty of opportunities for those interested in combining crystallography and photochemistry. More importantly, the combination of quantum chemical calculations with crystallography and photochemistry, should help in the understanding of weak interactions in solids, and predicting reactivity of molecules in the crystalline state.

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Electronic Supplimentary Information

All crystallographic data (CIF files) of published structures of seven reactive stilbazole.HCl salts (**1-5**, **7** and **8**) have been deposited previously with CCDC and their numbers are 813287-818801. Structures of unreactive *trans* crystals and the *cis* crystals have been solved and their CIF files are deposited with CCDC and their CCDC reference numbers are 1008122-1008125.

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