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Thiourea as a Template for Photodimerization of Azastilbenes

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Abstract: In this study we have explored the potential of thiourea (TU) as a template to preorient stilbazoles and bispyridylethylenes (azastilbenes) in the crystalline state. TU is able to preorient eleven azastilbenes toward dimerization in the crystalline state. While cocrystals of these eleven olefins photodimerized to a single dimer expected based on crystal packing, pure crystals of these olefins either were nonreactive or gave a mixture of dimers. The differential photobehavior of the pure crystals and cocrystals highlights the importance of TU in templating the olefins in a photoreactive orientation in the crystalline state. X-ray crystallographic and photochemical studies have identified a few azastilbenes that photodimerize in spite of not being arranged in an ideal orientation in the crystalline state. These as well as a few examples already reported in the literature suggest that it is important to recognize that molecules could experience large amplitude motions in the crystalline state, especially when energized by light. Short-term lattice instability caused by photoexcitation can be effective in driving a photochemical reaction. Thus one should view the crystalline arrangement of molecules upon light exposure as "dynamic" rather than "static" as determined from X-ray structure analysis.

Introduction

Photocycloaddition of olefins has proven to be a valuable synthetic tool to construct strained cyclobutane frameworks.[1,2] However, this approach works mostly with molecules where the $C{=}C$ bond is part of a relatively rigid cyclic system. In solution, when the $C{=}C$ bond is part of either an acyclic or a larger cyclic system ($>C_8$), [2 + 2] cycloaddition is unable to compete with facile geometric isomerization process. Furthermore, in solution [2 + 2] cycloaddition yields a stereoisomeric mixture of cyclobutanes, whose ratio depends on the Woodward−Hoffmann selection rules, electronic and steric factors and stability of diradical intermediates. The strategy of use of template molecules to align two olefinic molecules closer in a specific geometry favors a select dimer.[3−11] The pioneering study in this context due to that of de Mayo and co-workers templated enones at the aqueous−micellar interface to photodimerize them to a single dimer.[12−15] Recently, this approach has been extended to the use of well-defined water-soluble cavitands such as cyclodextrins, cucurbiturils, calixarenes, octa acid and Fujita Pd host.[16−27]

In contrast to solution chemistry, following the original discovery in 1871 by Libermann,[28] photodimerization in the solid state has been extensively explored with several elegant approaches. The topochemical postulation of Schmidt suggests "reaction in the solid state occurs with a minimum amount of atomic and molecular movement".[29,30] Accordingly, several strategies have been adopted to bring $C{=}C$ bonds of the reactive olefin pair within the required 4.2 Å and parallel conditions in the solid state so that they would dimerize upon excitation. This

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presentation is concerned with one such strategy, namely, "templation" in the solid state.

The "crystal engineering" approach initiated by Schmidt that has resulted in identification of chloro and fluoro groups, among others, as steering groups to close pack olefins within 4.2 Å requires structural modification of the olefin of interest.[31−34] A better approach using an independent molecule to steer olefins through noncovalent interactions, termed "templation", has been explored by a number of groups during the past two decades. Early reports on this topic came from the group of Toda, who used various diols to orient olefins through weak intermolecular hydrogen bonds.[35−40] They achieved photodimerization of chalcone, dibenzylideneactone, pyridones, coumarin, thiocoumarin and cyclohexenone in the solid state with the help of different diol templates for different olefins. A stronger Coulombic interaction between the template and the olefin was exploited to orient olefins by Ito, Scheffer and their co-workers for the same goal.[41,42] In this approach an olefin's acid group (e.g., cinnamic acid) was complexed with a diamine template (e.g., ethylene diamine) with the resulting salt orienting the olefins in the solid state toward photodimerization. This method is thus restricted to olefins containing either a COOH or NH_2 group.

The invaluable templating strategy has gained the attention of a number of groups recently. MacGillivray's group has identified 1,3-dihydroxybenzene as template to preorient 4,4′-bispyridylethylene (4,4′-BPE) toward dimerization in the crystalline state.[43,44] Vittal and co-workers reported a number of metal−organic coordination polymers based on the concept of templated phototodimerization of 4,4′-BPE.[45,46] In this context, one should also note that a few studies have expanded the strategy to include unsaturated dicarboxylic acids.[47−49] Literature reveals 4,4′-BPE to be a benchmark system to test the value of a molecule as a solid-state template.[50−54] The synthesis of ladderanes from 1,4-bis(4-pyridyl)-1,3-butadiene and 1,6-bis(4-pyridyl)-1,5-hexatriene in the solid state using substituted 1,3-dihydroxy-5-methoxybenzene as templates is a fine show and tell example.[55,56] In addition to weak interactions indicated above, confinement provided by well-defined host systems has also been exploited to template photodimerization in the solid state. In this context, studies in inorganic hosts such as zeolites and clays and organic hosts such as bis-urea and cucurbituril crystals are noteworthy.[57−63]

The above-reported hydrogen bonded templated strategy unfortunately suffers from the limitation that a minor variation in the structure of the olefin requires a corresponding one on the template as well. Finding a new template for each olefin (termed "template switching") is cumbersome. Although a universal template that would orient all olefins in the solid state may not be possible, identification of one that would steer more than a few olefins is worthwhile. Numerous templates have been reported for 4,4′-BPE. Thiourea (TU) fulfilled our interest in identifying a template that would orient olefins other than 4,4′-BPE. We begin the presentation with its use with 4,4′-BPE and continue with ten different 1-(4-pyridyl)-2-arylethylenes (stilbazoles; Scheme 1). A remarkable nine of the eleven investigated olefins were templated by TU in the solid state. As predicted by X-ray crystal structure they photodimerized to a single dimer in significant yields (80 to 100%). The C═C bonds of olefins **10** and **11** though oriented similarly to **3**−**9** were separated by more than 4.5 Å and expectedly were not reactive in the solid state. We close the presentation by disclosing our results on three more bispyridylethylenes (2,4′-BPE, 2,3′-BPE and 2,2′-BPE; **12**, **13** and **14** in Scheme 1), all of which photodimerized as TU cocrystals **12c**, **13c** and **14c**, respectively.

Results and Discussion

The present study consisted of the following aspects: crystallization and crystal structure analysis of the cocrystals of thiourea and olefins followed by irradiation and finally characterization of photoproducts. Analyses of Cambridge Structural Database (CSD) suggested that TU forms two types of hydrogen bonds with a guest molecule (type I and type II, Scheme 2b). We recognized that these structural motifs could be utilized to prealign olefins for photodimerization in the crystalline state. This has been realized in this study with fourteen different olefins. The methods of cocrystallization, procedures for irradiation and isolation of dimers, ^{1}H NMR data of dimers and

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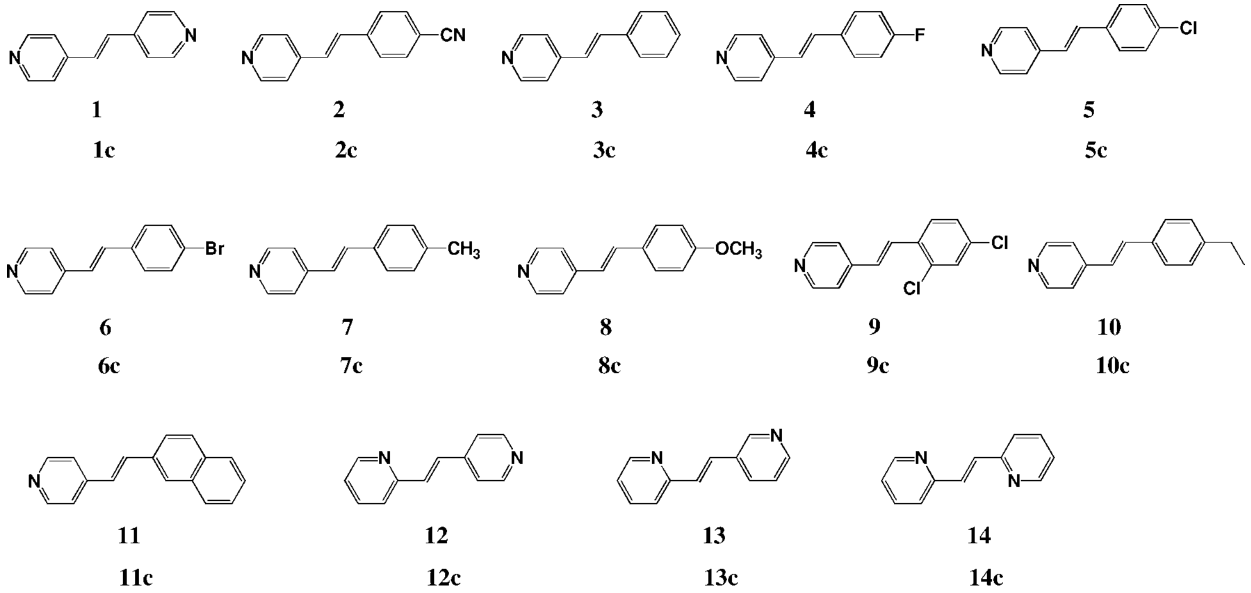
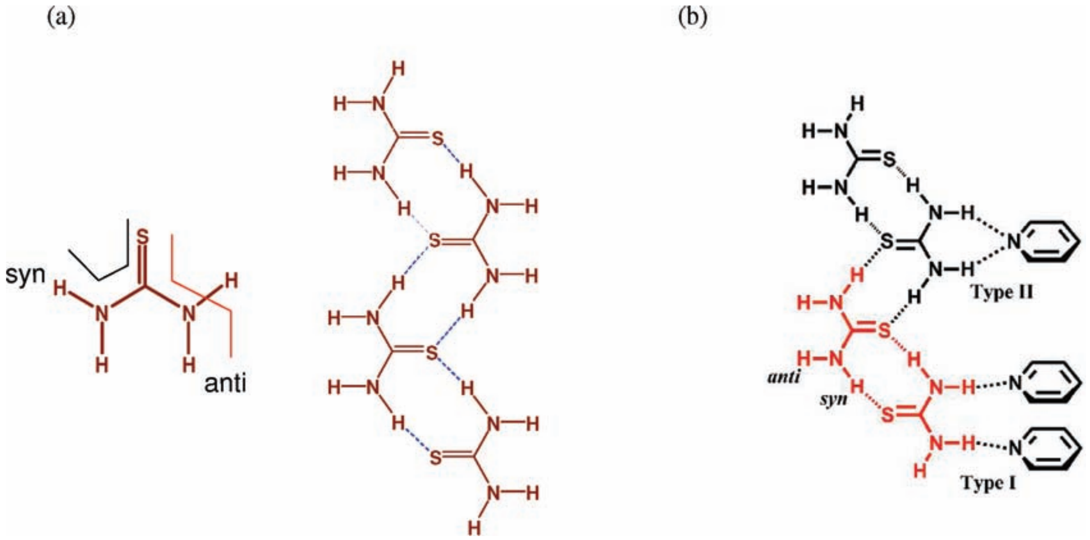
Scheme 1. Olefins and Their Thiourea Cocrystals Investigated in This Study[a]



[a] Olefins are numbered as **1**, **2**, etc. and TU cocrystals as **1c**, **2c** etc. See crystallographic analysis in the Supporting Information for ratio of individual components in cocrystals.

Scheme 2. Representation of Thiourea Tapes and Types of Hydrogen Bonds Thiourea Forms with Hydrogen Bond Acceptors



X-ray crystal structure analyses of cocrystals along with CIF files are provided in the Supporting Information.

Crystallographic Studies. As 4,4′-BPE is a benchmark example with several templates, we first tested if TU would preorient it toward dimerization in the solid state. Analysis by single crystal X-ray diffraction of 1:1 TU cocrystals of **1c** (Scheme 1) revealed that the structure contains a single molecule each of TU and 4,4′-BPE in the asymmetric crystal unit. As can be seen in Figure 1, TU through its two *anti* hydrogens interacts with the nitrogen atoms of **1**. One TU molecule interacts with two different molecules of **1**, and this helps to bring them closer. In addition, as expected, the *syn* hydrogens of TU interact with the sulfur atoms of the other TU molecules in the crystal lattice in a zigzag manner to form a one-dimensional tape. Interaction of TU tapes with 4,4′-BPE on both sides results in a two dimensionally ordered array as shown in Figure 1a. One could visualize the packing as a ladder where the BPE are the rungs and the TU tapes its arms. In this structure the molecules of **1** stack one on top of the other and the intermolecular packing distance for the 4,4′-BPE molecules affords their C═C bonds to be 4.15 Å apart, a value fulfilling Schmidt's topochemical criterion for photodimerization. Based on the packing derived from X-ray crystal structure analysis one would expect a *syn*-dimer to be formed.

The above packing arrangement prompted us to investigate 4-cyanostilbazole (**2**), a molecule which like **1** contains two nitrogen atoms (one pyridyl and one cyano) that can potentially hydrogen bond with TU. We anticipated **2** to orient similarly to 4,4′-BPE. The packing arrangement derived from X-ray crystal structure analyses of **2c** is shown in Figure 1b. Just as in **1c**, the *anti* hydrogen atom of two TU molecules on either side interacted with the pyridyl and cyano nitrogen atoms of two molecules of **2**. The molecules of **2** do stack one on top of the other in a parallel fashion leading to a head−head arrangement. In this assembly, the intermolecular packing distances

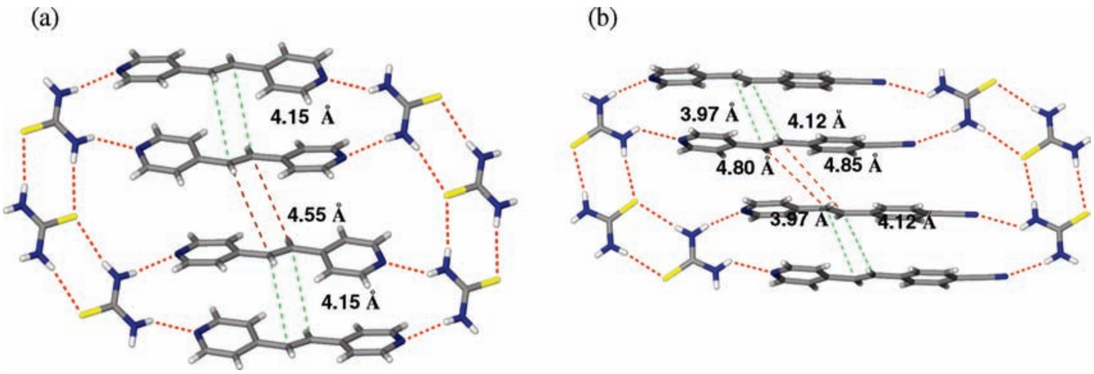


Figure 1. Packing arrangements of (a) TU·4,4′-BPE cocrystal (**1c**) and (b) TU·4-cyano stilbazole cocrystal (**2c**).

Table 1. N−H···N Distances and Angles for **1c** and **2c**[a]

cocrystal	N−H···N	*d* (Å) NH···N	*d* (Å) HN···N	∠N−H···N (deg)
1c (TU·**1**)	N(3)−H(3A) ···N(16A)	2.30	3.050(4)	146
	N(4)−H(4A)···N(5A)	2.21	2.989(4)	150
2c $(TU)_2 \cdot (\mathbf{2})_2$	N(3)−H(3A) ···N(9A)	2.43	3.045(3)	130
	N(4)−H(4A)···N(25A)	2.10	2.944(3)	169
	N(7)−H(7A)···N(40A)/CN	2.51	3.095(4)	126
	N(8)−H(8A)···N(24A)/CN	2.26	3.104(2)	165

[a] N−H refers to thiourea and N to pyridyl ring.

between the C═C carbon atoms are 3.97 Å and 4.12 Å, within the topochemical limit for photodimerization.

Examination of the packing arrangements of **1c** and **2c** (Figure 1) suggests that, when there are two hydrogen bonding centers in the guest olefin, the preferred packing is likely to be the ladder type with TU tapes serving as arms. In this context, TU behaves similarly to 1,3-dihydroxybenzene, 1,8-naphthalene dicarboxylic acid, Rebek's imide, and 1,2,4,5-tetracraboxylic acid where a single template molecule through hydrogen bonding to two molecules of 4,4′-BPE brings them within Schmidt's topochemical distance.[43] The difference between TU and the templates mentioned above is that TU forms a tape holding several guest molecules like the rungs of the ladder while the others act as an independent 2:2 host to guest complex. Thiourea forms an infinite tape structure in which the azastilbene molecules are held within reactive distance. In this context thiourea as a template differs from the well-examined resorcinol where two molecules of template hold two molecules of the olefin. The tape formed by thiourea is comparable to urea and 3-aminophenol reported in the literature.[64,65]

In **1c** and **2c**, TU templates the reactants by relatively weak N−H···N hydrogen bonding interactions rather than strong O−H···N interactions or strong metal−ligand interactions. The distance between two N−H donors in a TU molecule is about 2.3 Å, which is shorter than the $\pi-\pi$ stacking distance between two reactant molecules. Therefore, the hydrogen bond interactions (type I) linking the pyridine and cyano groups to the TU template in **1c** and **2c** are bent (see the last column in Table 1). This most likely results from forced short distance between π clouds of the two olefins. A list of these N−H···N interactions is provided in Table 1.

Having established the ability of TU to template 4,4′-BPE in the solid state, we proceeded to investigate, more importantly, if it can template olefins containing only one hydrogen bonding atom. In this context we investigated nine *trans*-1-(4-pyridyl)-2-arylethylenes (Scheme 1). To our knowledge no attempts to steer stilbazoles in the crystalline state have been reported except for those by MacGillivray's group on 4-chlorostilbazole and stilbazole where *syn* head−head dimers resulted through templation with resorcinol and Ag ion respectively.[66,67] We were pleased to find TU capable of templating seven of the nine stilbazoles we investigated toward *anti* head−tail dimers. The packing arrangements for all nine stilbazoles are identical (*anti* head−tail) although in two the distance between the reactive olefins exceeded the Schmidt's topochemically allowed distance for photodimerization.

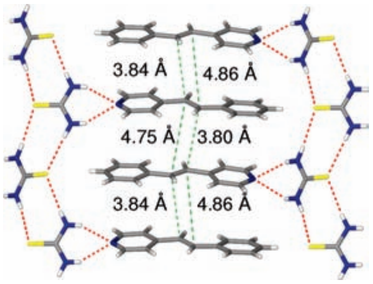


Figure 2. Packing arrangements of TU cocrystal with stilbazole **3**.

Packing arrangement obtained from single crystal X-ray analysis of **3c** containing only one hydrogen-bonding atom (on the reactive olefin **3**) is shown in Figure 2 (note the different packing arrangements for **2c** and **3c** in Figures 1b and 2). Notably it is important to point out that stilbazole forms type II hydrogen bonding (Scheme 2b) with TU tape (Figure 2). In this two dimensionally ordered system, the stilbazoles do stack one on top of another but with a head to tail orientation. This can also be viewed as the molecules of **3** are interdigitated between two TU one-dimensional tapes (Figure 3). A similar packing pattern was noticed with **4c**−**11c** (Figures 4 and 5). The maintenance of the head−tail alignment with even **9c** suggests that the dichloro substitution often used to align olefins in a head−head fashion was offset by hydrogen bonding by the TU template.[34] In cocrystals **3c**−**9c** the reactive carbon atoms of C═C bond are within 4.2 Å and in the remaining two cases (**10c** and **11c**) more than 4.4 Å apart. Based on packing arrangements one would expect *anti* head−tail dimers from **3c** to **9c**.

We were then interested in probing TU's ability to template bispyridylethylenes other than the benchmark 4,4′-BPE. In this context we examined 2,4′-, 2,3′- and 2,2′-bispyridylethylenes (2,4′-

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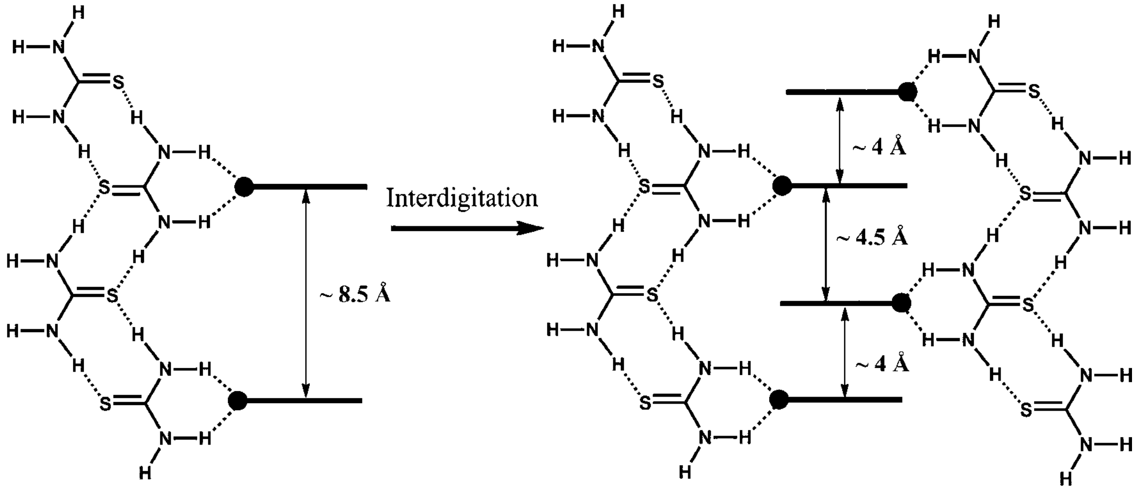


Figure 3. Interdigitation of thiourea−stilbazole tapes results in head−tail orientation of reactive stilbazole units. Note the reactive olefins are held by different thiourea tapes.

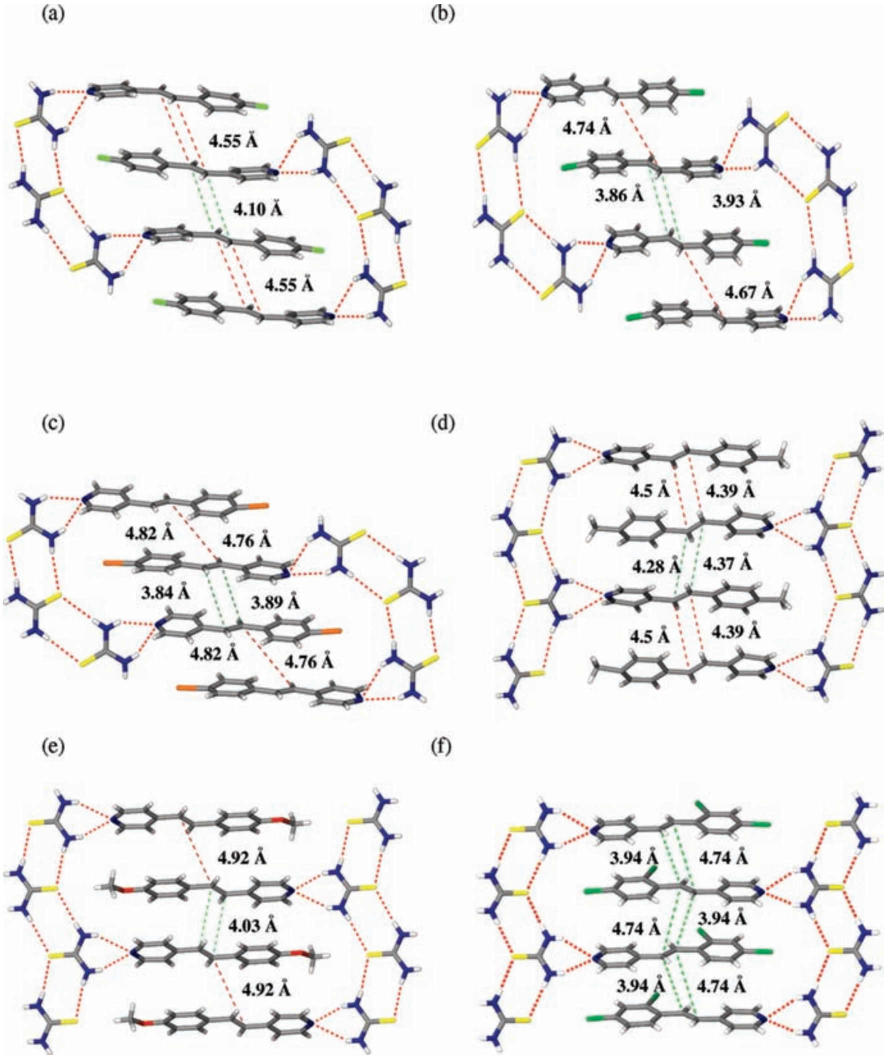


Figure 4. Packing arrangement of stilbazole (a) **4**, (b) **5**, (c) **6**, (d) **7**, (e) **8** and (f) **9** in TU cocrystals.

BPE, 2,3′-BPE and 2,2′-BPE respectively). All three BPEs gave 2:1 (TU to BPE) cocrystals from appropriate solvents (see Table S4 in SI). Examination of the packing arrangements for TU cocrystals with these BPEs shown in Figure 6 reveals a similarity between packings of the former two (2,4′-BPE, 2,3′-BPE) with those of TU-stilbazoles shown in Figures 2, 4 and 5 and would be expected to yield *anti* head−tail dimer. With a unique packing arrangement where the parallel C═C bonds are separated by 8.16 Å, TU-2,2′-BPE cocrystal would not be expected to dimerize.

Photochemistry of TU-Bispyridylethylene and TU-Stilbazole Cocrystals. Procedures for irradiation, isolation and identification of products are provided in Supporting Informa-

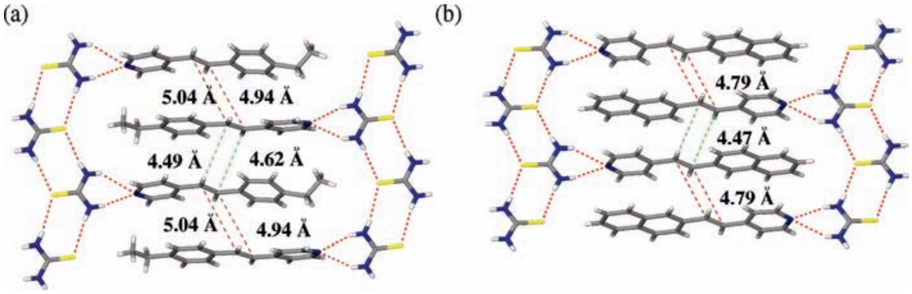


Figure 5. Packing arrangement of stilbazole (a) **10** and (b) **11** in TU cocrystals.

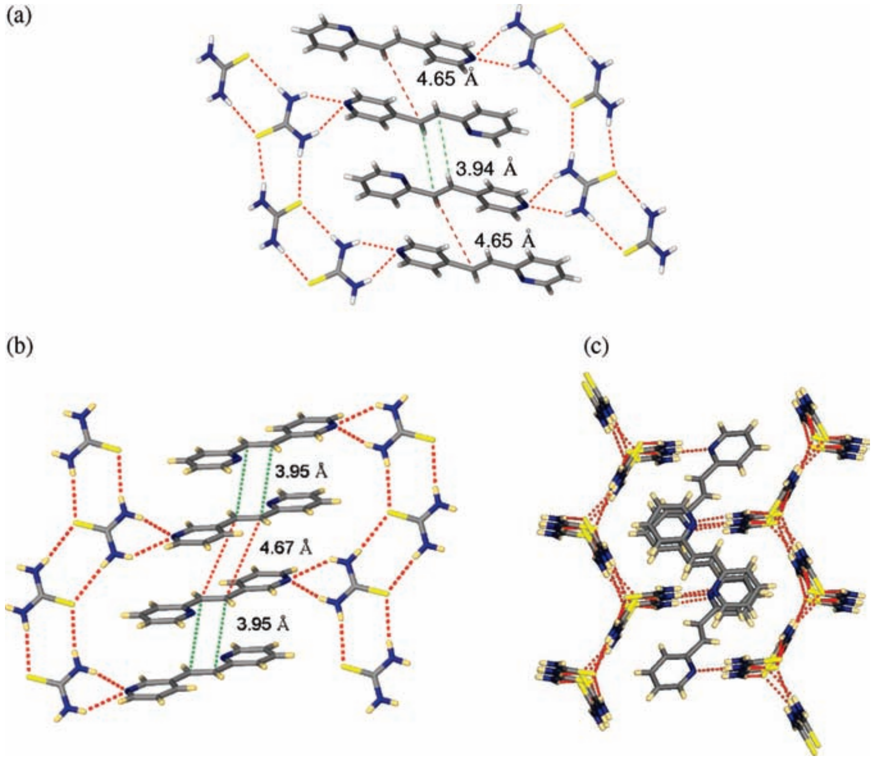


Figure 6. Packing arrangement of (a) 2,4′-BPE (**12**), (b) 2,3′-BPE (**13**) and (c) 2,2′-BPE (**14**) in TU cocrystals.

tion. Briefly, samples of about 8−10 mg of powdered single crystals of TU-olefin cocrystals **1c**−**14c** spread uniformly between two Pyrex glass plates over 10−15 cm^2 area and sealed with parafilm were irradiated (>290 nm). For uniform irradiation the samples were turned around every 4 h and respread between the plates every 8 h and generally irradiated for 24 h. Irradiation was discontinued after 12 h in the few cases where the samples became powdery or gummy. The progress of the reaction was monitored by recording ^{1}H NMR, in DMSO-d_6, of a small amount of the sample taken from the above irradiations. Upon reaction completion the samples were taken in D_2O and extracted with $CDCl_3$ to obtain ^{1}H NMR spectra of the products. At this stage all TU was removed from the product. Crystallographic details, stereochemistry and yields of dimers are provided in Table 2. Reactivity and the structure of the dimer are consistent with the packing arrangement shown in Figures 1, 2, 4, 5 and 6. As expected, the cocrystals **10c** and **11c** were unreactive (see Figure 5).

Irradiation of powdered **1c** gave a single product that was identified to be the *syn*-dimer (**15**, Scheme 3) by ^{1}H NMR and comparison with authentic sample. According to ^{1}H NMR no other products were formed and the reaction was clean. The conversion could not be taken beyond 90% as the crystallinity was lost with the progress of photodimerization. Irradiation of powdered cocrystals of **2c** gave a single product identified to be the *syn* head−head dimer (*syn* HH; **16**, Scheme 3) by ^{1}H NMR. As per ^{1}H NMR no other products were present; the reaction was clean and reached 100% conversion in 18 h of irradiation. Cocrystals **3c**−**8c** gave *anti* head−tail (*anti* HT, **17**, Scheme 3) as the single product in each case (see Supporting Information for the ^{1}H NMR spectra). In all examples the yield of the dimer was >90%. While cocrystals of olefins **1c**−**8c** photodimerized to a single dimer, pure crystals of the olefins **1**−**8** either were nonreactive or gave a mixture of dimers.

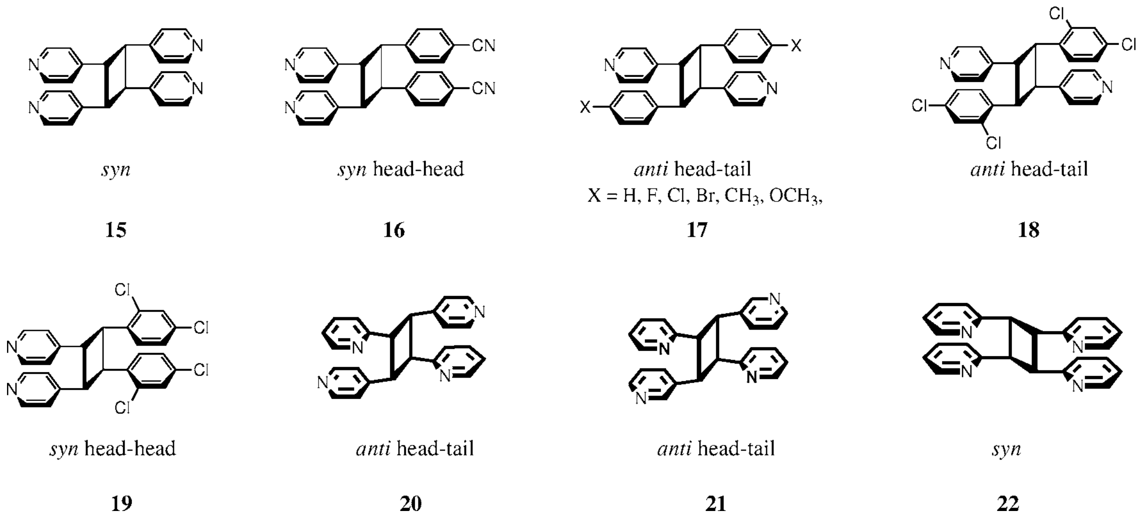
Perusal of Table 2 reveals the photobehavior of **9c** to be different from what would be predicted based on the packing pattern shown in Figure 4f. Unlike the expected single dimer, namely *anti* head−tail, a mixture of *anti* head−tail and *syn* head−head dimers (**18** and **19**, Scheme 3) was obtained. We believe that *syn* head−head dimer most likely results from pure crystals of **9** that are present along with **9c**. To ascertain this, single crystals of **9** were irradiated and its structure was obtained by X-ray crystal structure analysis. Consistent with the packing arrangement for **9** provided in Supporting Information, irradiation of its crystals gave *syn* head−head dimer in quantitative yield. Our attempts to obtain pure crystals of **9c** were not successful. This was probably due to the ability of compound **9** to readily crystallize independently rather than as cocrystals.

Table 2. Packing Details in Cocrystals **1c**−**14c**. Dimerization Yield and the Nature of Dimer are also Included

cocrystal number	space group	no. of symmetry independent azastilbenes in AU	disorder ratio	overall parallel parallelism[a] (%)	dimer yield[b] (%)
TU·**1** **1c**	$P2_1/n$	1	78:22	100	~90%
(TU)$_2$·(**2**)$_2$ **2c**	$P2_1/c$	2	(1) 91:9; (2) ~90:10 (not modeled)	~9−20%	~100 *syn* HH
(TU)$_4$·(**3**)$_4$ **3c**	Pn	4	(1) 56:44; (2) 80:20; (3) no disorder; (4) no disorder	32	~100 *anti* HT
TU·**4** **4c**	$P2_1/c$	1	56:44	100	~100 *anti* HT
TU·**5** **5c**	$C2/c$	1	60:40	80	~100 *anti* HT
TU·**6** **6c**	$C2/c$	1	59:41	82	~100 *anti* HT
(TU)$_2$·(**7**)$_2$ **7c**	$P2_1/c$	2	(1) 51:49; (2) 57:43	94	~98 *anti* HT
(TU)$_2$·(**8**)$_2$ **8c**	$P\bar{1}$	2	(1) 86:14; (2) no disorder	100	~90 *anti* HT
TU·**9** **9c**	$Pna2_1$	1	no disorder	0	~80[c] *anti* HT + *syn* HH
(TU)$_2$·(**10**)$_2$ **10c**	$P2_1/c$	2	(1) 50:50; (2) 77:23	73	no reaction
(TU)$_2$·(**11**)$_2$ **11c**	$P\bar{1}$	2	(1) 76:24; (2) no disorder	100	no reaction
(TU)$_2$·(**12**)$_2$ **12c**	$P\bar{1}$	1	84:16	100	100
(TU)$_2$·(**13**)$_2$ **13c**	$P\bar{1}$	1	82:18	100	100
(TU)$_2$·(**14**)$_2$ **14c**	$P2_1/c$	1	no disorder	0	~30% from bulk sample

[a] Overall parallel alignment of olefinic groups of reacting pairs in a cocrystal was calculated as outlined below with **3c** as an example. Of the four symmetry independent olefin molecules present in an asymmetric unit two are disordered. These four olefin molecules form two reacting pairs (two disordered molecules forming one pair and the two non-disordered molecules forming the second pair). In the disordered set 56% (major part) of first molecule (see values in the table) is parallel with 20% (minor part) of second molecule and 44% (minor part) of first molecule is parallel with 80% (major part) of the second molecule. In this pair 36% [(36 + 36)/200] of the molecules remain crossed. In the non-disordered pair the olefinic bonds are crossed (100%). Overall (combination of two sets) 68% [(36 + 100)/(100 + 100)] of molecules are crossed and 32% of molecules are parallel. [b] The photodimerizations are completed approximately between 15 and 30 h. [c] In **9c** the dimerization went up to 80% in about 36 h (the sample was mixed and spread between the Pyrex plates and monitored by ^{1}H NMR after every 5 h). Mixture of *anti* HT and *syn* HH dimers was obtained in 55:45 ratio. The reason for the formation of a mixture of isomers could be attributed to the presence of uncomplexed **9** along with **9c** where the former one yields *syn* HH dimer upon photoexcitation (see Figures S10 and S19).

Scheme 3. Structures of Photoproducts



Excepting **9c**, no other cocrystals, **1c**−**8c**, were contaminated with pure olefin crystals, **1**−**8**.

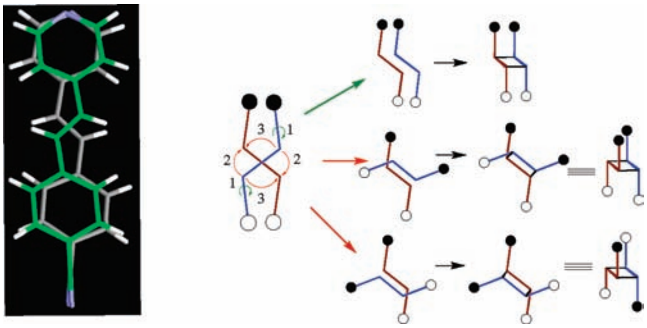
Irradiation of crushed TU cocrystals with 2,4′- and 2,3′-BPE gave *anti* head−tail dimers (**20** and **21**, Scheme 3) as the single product (see Supporting Information for ^{1}H NMR). Quantitative conversion to product was achieved in about 20 h. As expected based on packing arrangement crystals of **14c** were photoinert. However, irradiation of ground powder of TU and 2,2′-BPE in the ratio of 2:1 gave quantitatively *syn*-dimer (**22,** Scheme 3). X-ray quality single crystals of these complexes could not be obtained. We believe that the reactive form must be a different polymorph of the cocrystal whose structure is presented in Figure 6.

In conclusion, we have been able to preorient twelve bispyridylethylenes and stilbazoles toward dimerization in the solid state with a single template, TU. While cocrystals of these olefins photodimerized to a single dimer expected based on crystal packing, pure crystals of these olefins either were nonreactive or gave a mixture of dimers. The differential photobehavior of the pure crystals and cocrystals highlights the importance of TU in templating the olefins in a photoreactive orientation in the crystalline state. Examination of packing arrangements shown in Figures 1, 2, 4, 5 and 6 and the crystallographic data provided in Table 2 suggests that not all olefins are packed in an ideal geometry as required by topochemical postulate: for example, the C═C bonds in reactive pairs are criss-crossed in some (**2c**, **3c** and **9c**) and the two ends of the reactive C═C not equidistant in others (see **5c**, **6c**, **7c**); the photodimerization nevertheless occurs up to at least 90% conversion.

Photodimerization under Less than Ideal Topochemical Conditions. It is important to note that the olefin pairs in most cocrystals investigated in this study were disordered over two orientations. The disorder was modeled during the crystallographic analysis. Details of refinement and disorder treatment are provided in Supporting Information. In addition to the disorder problem, the C═C bonds in reactive pairs of olefins in TU cocrystals **2c**, **3c** and **9c** although within 4.2 Å are criss-crossed (see Table 2 for details). In Table 2 this is given as "extent of parallel arrangement". While, in **2c** and **3c**, the percentage of molecules that are not parallel is in the range of 68 to 80%, in the case of **9c** all molecules are criss-crossed. Yet these olefins are reactive. Several such examples have come to light since the original formulation of topochemical postulate by Schmidt.[68−71] A few molecules where the C═C bonds are not parallel and the distances are more than 4.2 Å have been reported to react. Similarly, there are examples where the reactive pairs being within 4.2 Å were photoinert.[72,73] Since the formulation of Schmidt's topochemical postulate it has become clear that molecules in a crystal undergo various types of motions at room temperature and some of these could aid photoreactivity in the solid state.[74,75] However, it is important to note that some of these motions occur only upon activation of molecules to the excited state and do not occur at room temperature in the absence of light.

Doubt on the generality of the postulate that large motions would not be tolerated in a single crystal has been raised by the discovery of several photochemically initiated *cis*−*trans* isomerizations of olefins in crystals.[76−78] *Cis*−*trans* isomerization requires much larger motion than the one required to bring non-topochemically aligned olefin pairs toward dimerization. Occurrence of *cis*−*trans* isomerization in crystals suggest that, as long as the surrounding molecules allow, even the criss-crossed pair could photodimerize by adopting a parallel arrangement upon excitation. This expectation is along the lines of a suggestion originally put forward by Craig and co-workers that a reaction not expected based on ground state structure may indeed occur if localized excitation of a molecular crystal produces instability of the lattice configuration.[79,80] This instability that could result in large displacements from the original lattice structure could lead to a photoreaction unexpected based on ground-state topochemical postulate. Thus even in systems where the molecules are not fully prealigned, dimerization could occur as long as two molecules are close to each other and the neighboring molecules allow modest molecular motion of the excited molecule in the crystal.

Scheme 4. Various Motions That Could Bring the Criss-Crossed C═C Bonds to Parallel Arrangement[a]



[a] Simultaneous rotation marked as 1 is the pedal-like rotation of one of the two C═C bonds. Markings 2 represent clockwise in-plane movement of one of the two C═C bonds. Markings 3 represent anti-clockwise in-plane movement of one of the two C═C bonds.

In the case of **2c** and **3c**, more than 65% reactive pairs are criss-crossed (Table 2). In spite of such an unfavorable arrangement, **2c** gave *syn* head−head dimer and **3c** gave *anti* head−tail dimer in quantitative yield. However, **9c** where all reactive pairs are criss-crossed gave a mixture of *anti* head−tail dimer (see Supporting Information for ^{1}H NMR spectra). As illustrated in Scheme 4, one could visualize two possibilities of bringing the criss-crossed pair to parallel arrangement. In the first possibility, one of the two molecules displaces along the molecular plane as visualized in the case of 7-methoxycoumarin, a motion that could occur in either a clockwise or an anticlockwise manner.[81] The other possibility is a pedal-like motion of one of the two molecules. Occurrence of pedal-like motion even in the ground state of stilbene-like molecules has been well established.[82,83] Such motion has been invoked during templated photodimerization of *trans*-cinnamide and *trans*-2,4-dichlorocinnamic acid.[70,71] Thus, occurrence of both types of motion has precedence. Depending on the above two motions different isomers would result as is illustrated in Scheme 3 for **2c**. Quantitative yield of only the *syn* head−head dimer from **2c** suggests the dimerization to be facilitated by pedal-like motion and not lateral displacement. Similar arguments could be made for **3c** and **9c**.

One question that remains to be resolved is whether the pedal motion occurs before or after excitation. While in **9c** it must

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occur upon excitation, in **2c** and **3c** a small fraction of molecules that are oriented properly could absorb the light to yield the dimer. As the dimerization proceeds more could reorient themselves toward the product dimer. One should also note that only one of the two molecules in a reactive pair has to undergo the pedal motion to become parallel. Further in depth understanding of the mechanism of photodimerization of non-topochemically oriented olefins would require time-resolved X-ray crystallographic investigations that we hope would be performed in the near future.[84−88]

Summary

We close the presentation by pointing out that the topochemical postulate should be considered a guideline rather than a rule. If large amplitude molecular motions are possible in the crystalline state, especially when energized by light, photodimerization from criss-cross olefins should not be a surprise. In this study we have identified thiourea (TU) as a useful template to orient bispyridylethylenes and stilbazoles toward photodimerization. We are pleased that we were able to preorient 11 of the 14 olefins investigated toward photodimerization in the crystalline state. Even the two that did not dimerize were packed similarly to other stilbazoles but with more than 4.5 Å distance between the reactive C═C bonds. Most mechanically ground TU-olefin cosolids showed photochemical behavior similar to that of single crystals of TU-olefin cocrystals. We are currently pursuing this aspect of solid-state photochemistry.

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Supporting Information Available: Experimental procedures, X-ray crystallographic data, CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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