

# Supramolecular Photochemistry

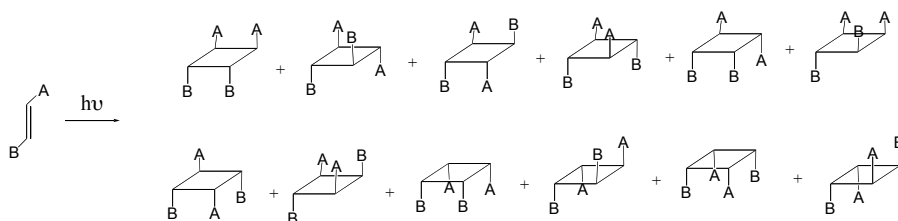
## Controlling photochemical reactions through templation

### Concept

### Examples

1

In the absence of control photoaddition leads to multiple products

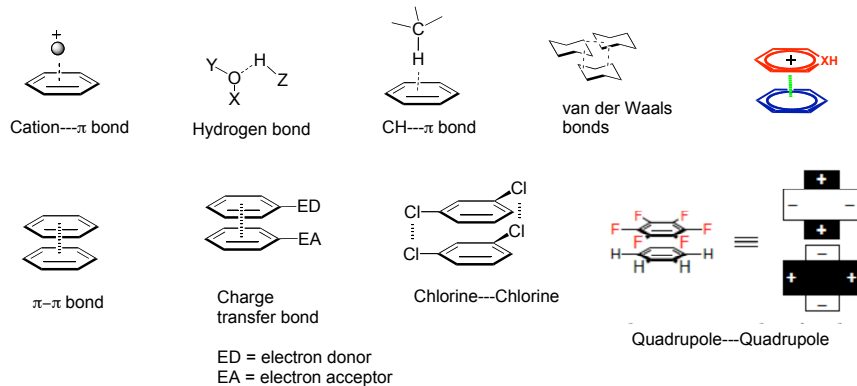


- Multiple products with different stereo and regiochemistry possible (assuming no electronic or steric preference).
- Pre-organization is essential to achieve selectivity. The cost for selectivity should be pre-paid, *i.e.*, system should be entropically prepared

2

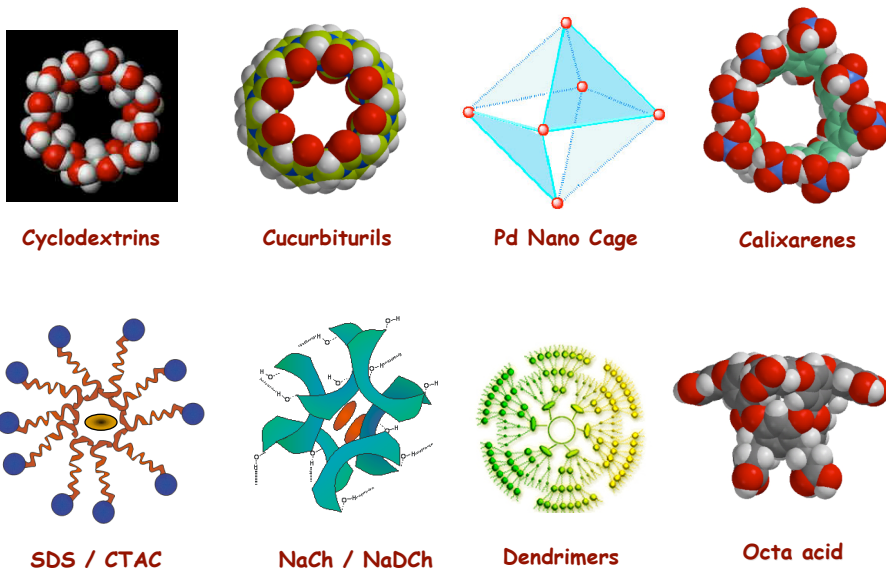
## Weak interactions often utilized in templation

Examples of weak intermolecular bonds (typical energies vary from  $< 1 \text{ kcal mol}^{-1}$  to  $\sim 10 \text{ kcal mol}^{-1}$ )



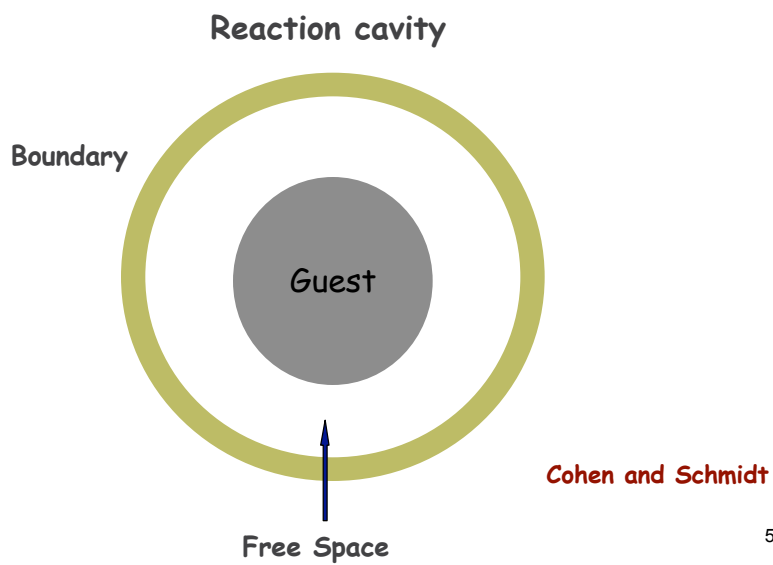
3

## Water Soluble Hosts as Confining Media



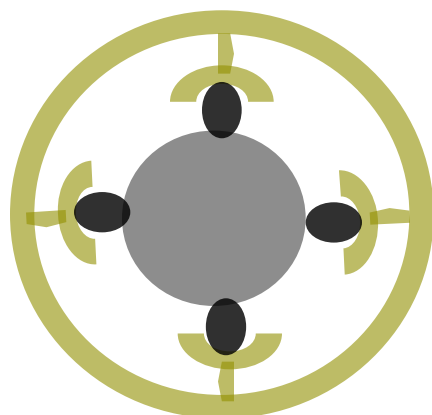
4

## Concept of Reaction Cavity



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## Role of Weak Interactions



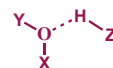
Cation--- $\pi$



$\pi$ --- $\pi$



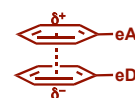
C-H--- $\pi$



Hydrogen bond



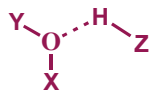
van der Waals



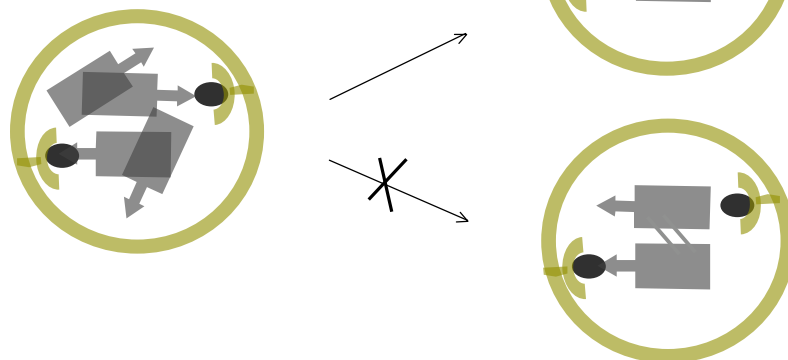
Charge transfer

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## Pre-organization Through Weak Interactions

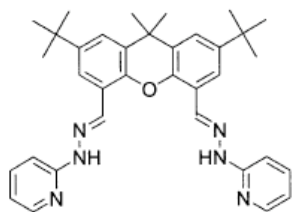
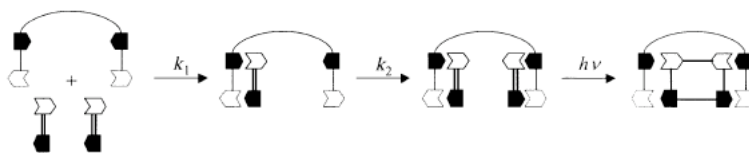


Hydrogen bond

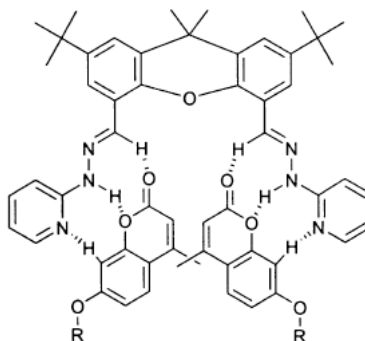


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## Templation in solution through hydrogen bonding



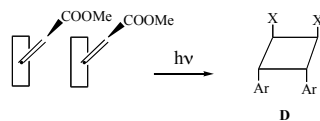
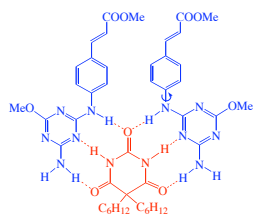
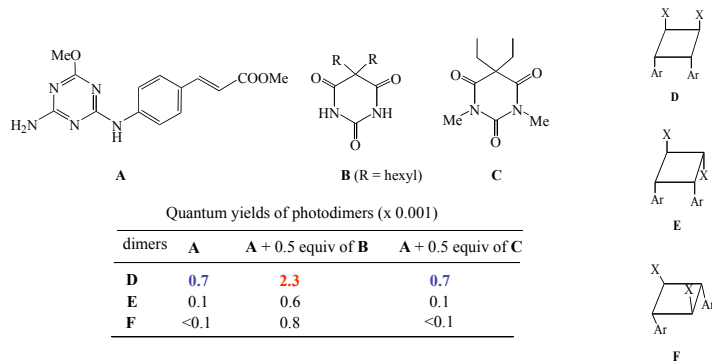
Host



Guest templated by host

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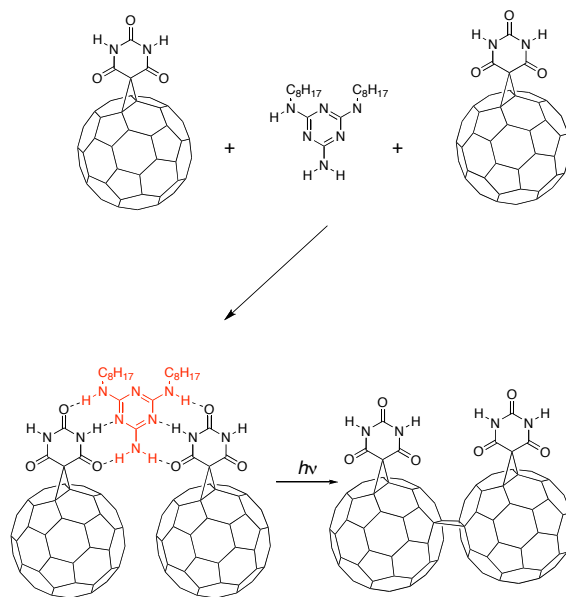
## Templation in solution through hydrogen bonding



Isomerization slowed; dimerization enhanced

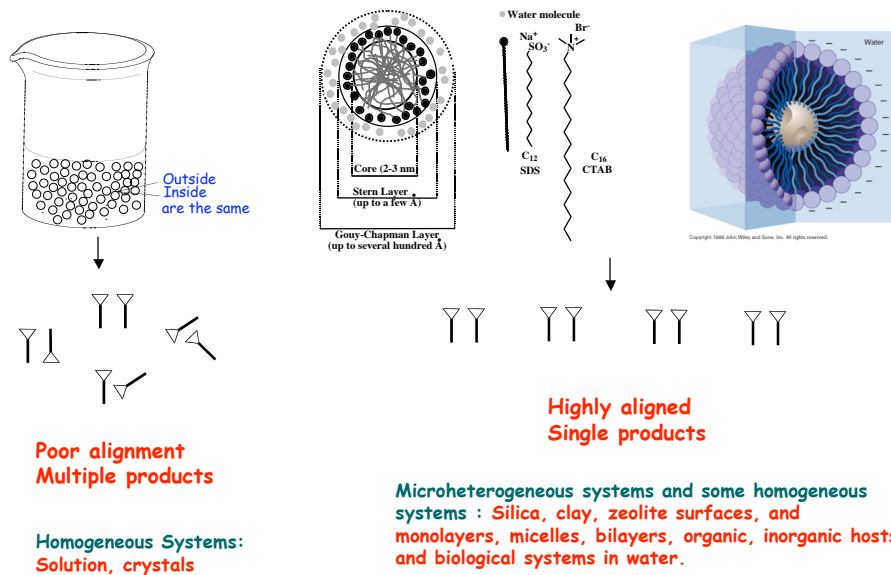
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## Templation in solution through hydrogen bonding



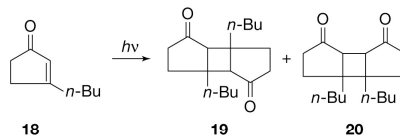
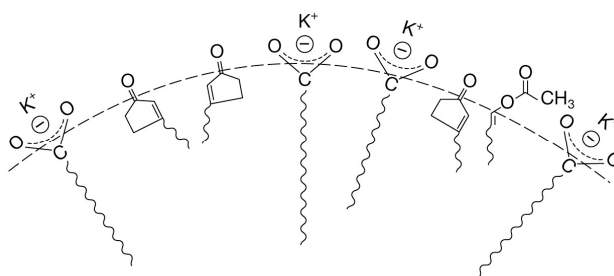
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## Interface helps to orient reactant molecules



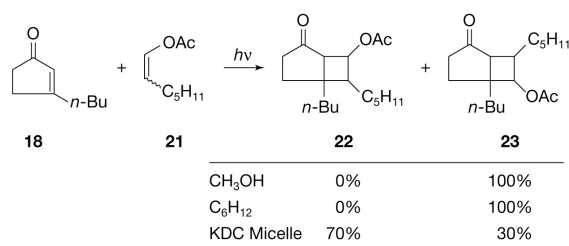
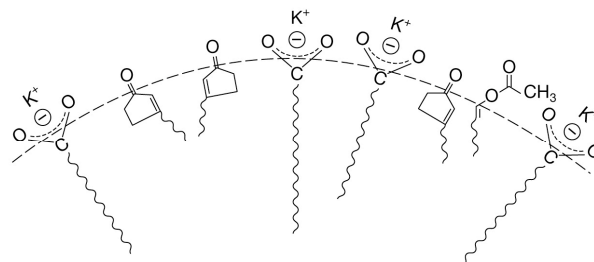
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## Templation in water with the help of an organized assembly



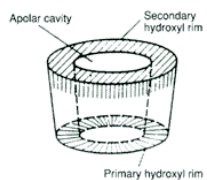
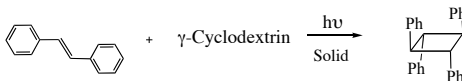
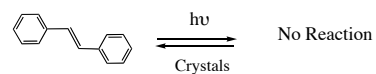
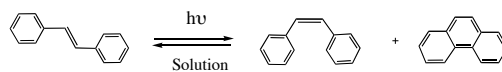
C <sub>6</sub> H <sub>6</sub>	91%	9%
C <sub>6</sub> H <sub>12</sub>	96%	4%
KDC Micelle	2%	98%

## Templation in water with the help of an organized assembly



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## Templation with the help of an organic host: Cyclodextrins



Oligosaccharides consisting of 6 or more  $\alpha$ -1,4-linked D-glucose units

Volume ( $\text{\AA}^3$ ): 176 ( $\alpha$ ), 346 ( $\beta$ ), 510 ( $\gamma$ )

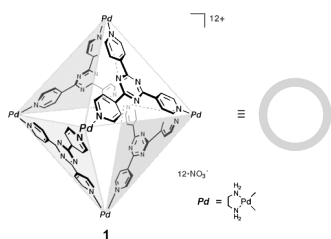
Dia at the larger end ( $\text{\AA}$ ):  
8.8 ( $\alpha$ ), 10.8 ( $\beta$ ), 12.0 ( $\gamma$ )

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## Templation with the help of an inorganic host: Fujita pd host



R = OEt	0%	92%	0%
OMe	6%	44%	22%
H	21%	35%	14%



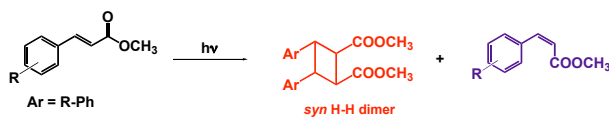
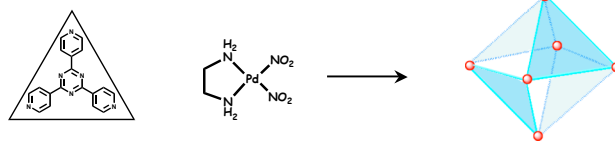
Interior dia ~ 30 Å  
Interior hydrophobic  
Water soluble

In the absence of host only acenaphthylene dimer; no cross dimer

Preferential inclusion of A and B.

Size controlled inclusion.

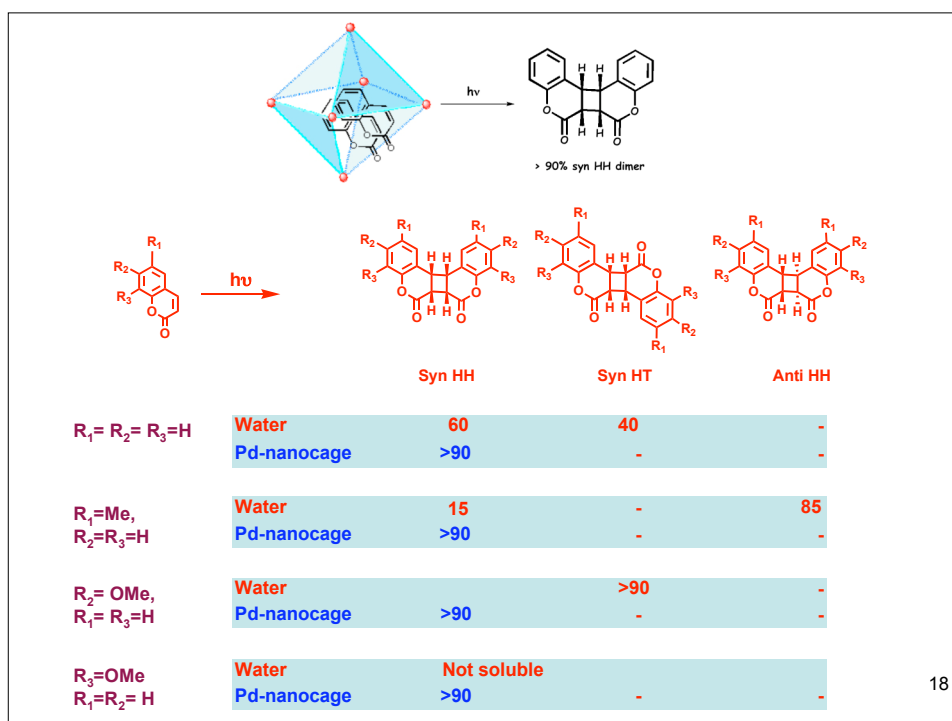
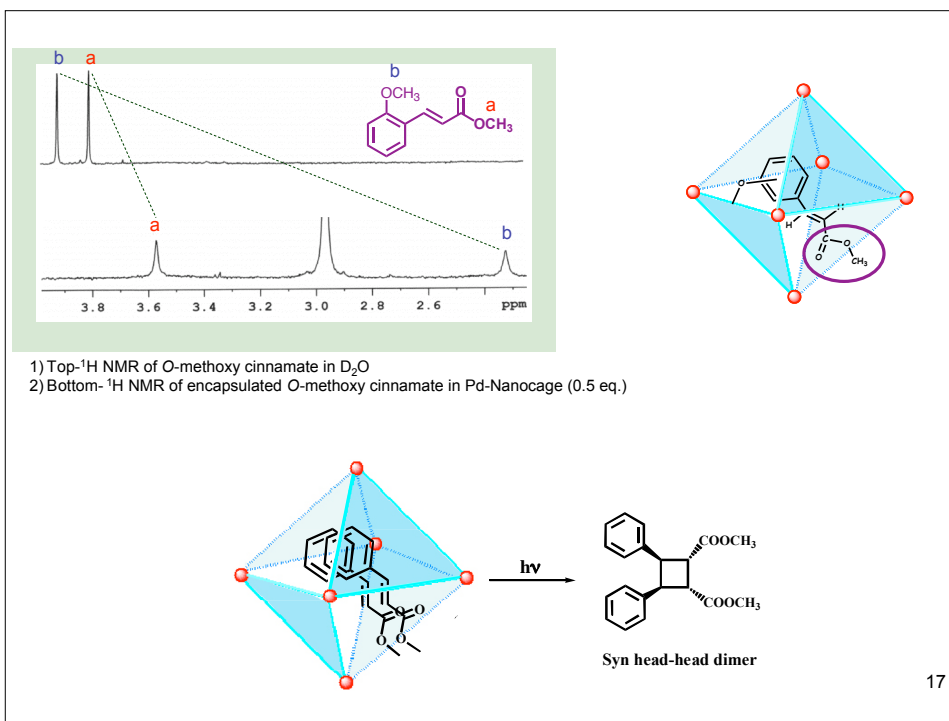
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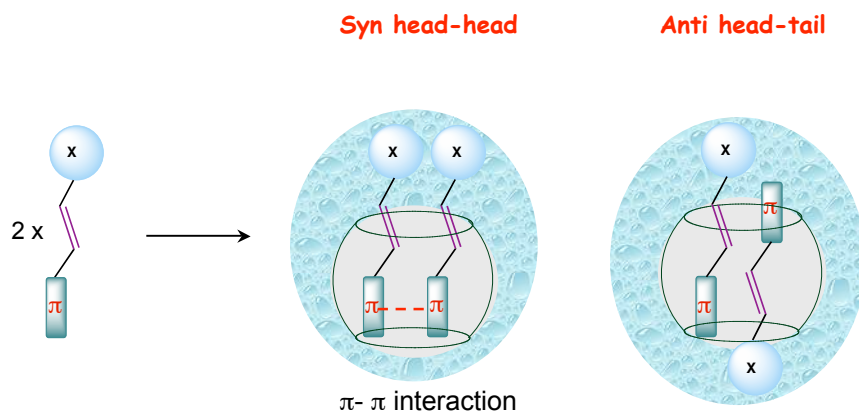
Substrate	% of Syn H-H dimer in nanocage	% of cis isomer
	63	37
	45	55
	42	58
	40	60

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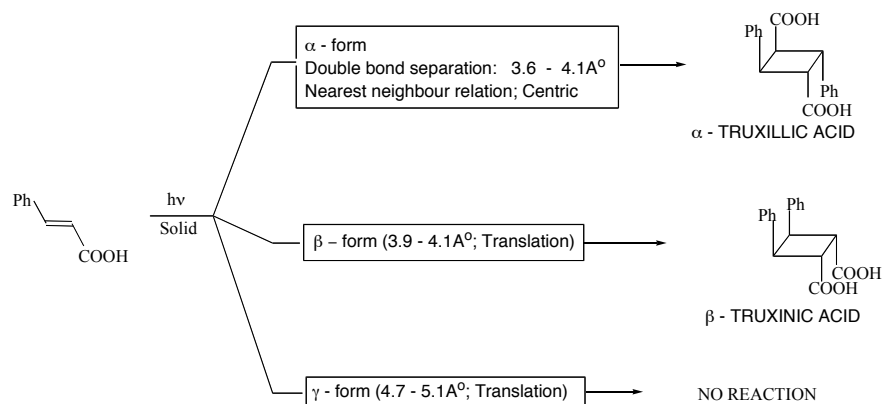


## Templating with the help of an organic host: Cucurbiturils



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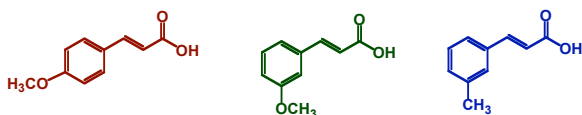
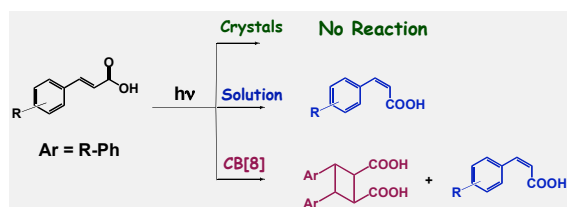
## Schmidt's generalization of solid state reactions



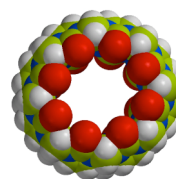
**Topochemical principle: Reactions in the solid state take place with minimum atomic movements.**

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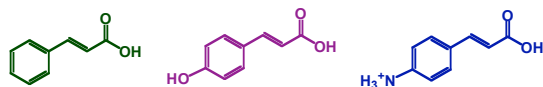
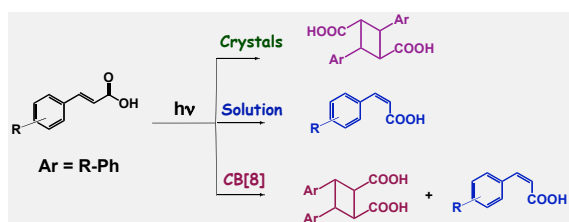
**trans-Cinnamic acids photo inactive in solid state ( $\gamma$ -form)**



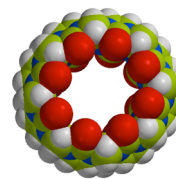
Ar	Solid state	% of dimer in CB[8]	% of cis isomer
R=4-OCH <sub>3</sub>	--	72	28
R=3-OCH <sub>3</sub>	--	72	28
R=3-CH <sub>3</sub>	--	83	17

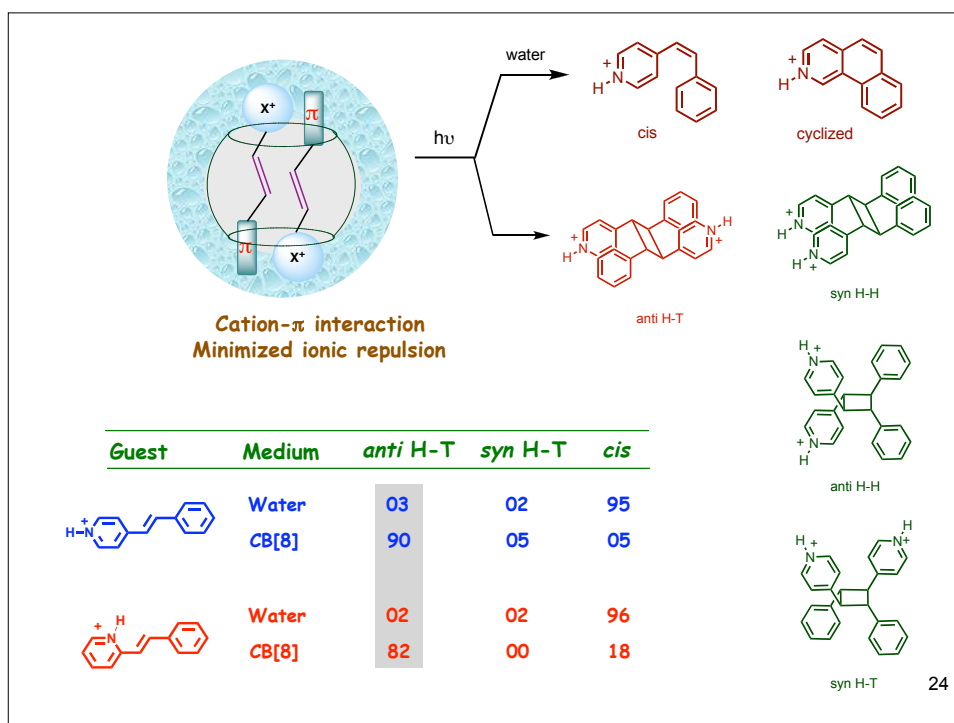
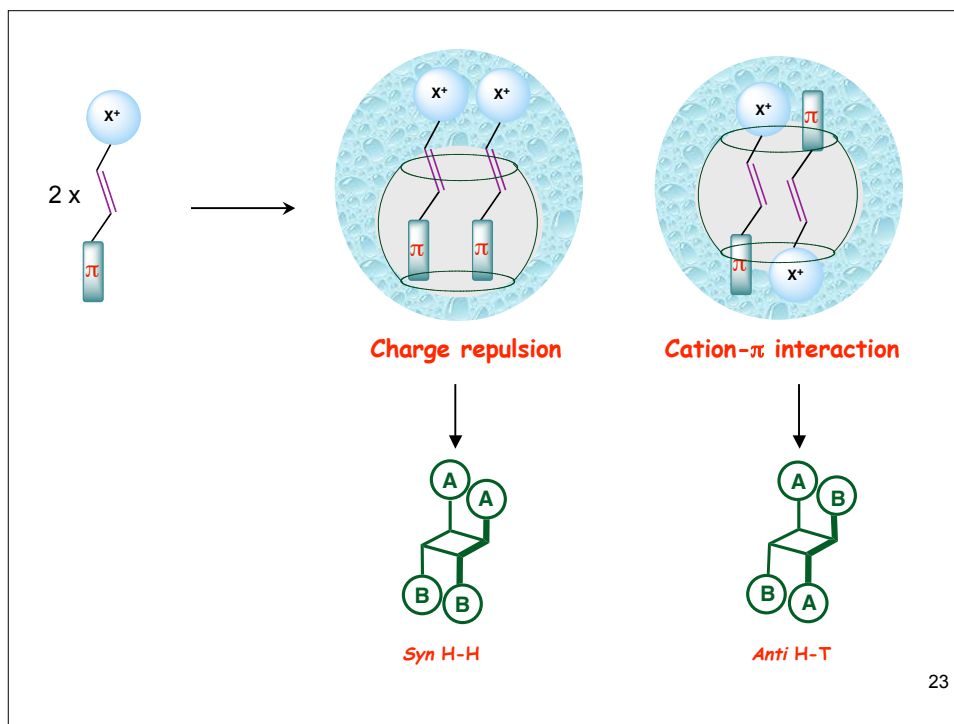


**trans-Cinnamic acids that yield anti H-T dimer upon irradiation in solid state ( $\alpha$ -form)**

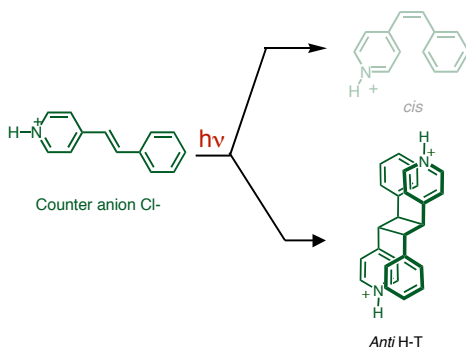


Ar	Solid state % of anti H-T dimer	% of Syn H-H dimer in CB[8]	% of cis isomer
R=H	100	54	46
R=4-OH	100	38	62
R=4-NH <sub>3</sub> <sup>+</sup>	100	88	12

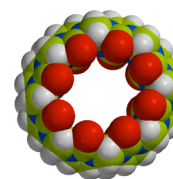
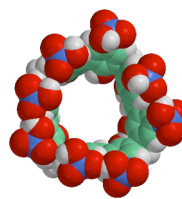
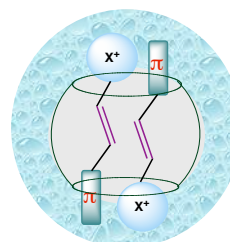




## Photochemistry of Stilbazoles

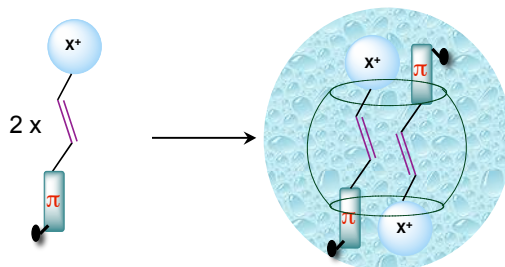


Medium	<i>anti</i> H-T	<i>syn</i> H-T	<i>cis</i>
dil. HCl	13	16	71
PHBSA	24	14	62
CA[6]SO <sub>3</sub> H	76	5	19
CA[8]SO <sub>3</sub> H	86	2	12
CB[8]	90	--	10

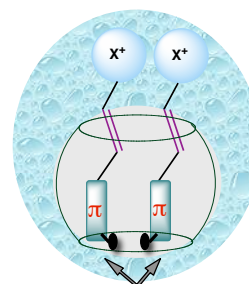


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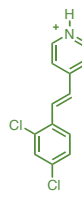
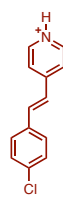
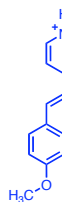
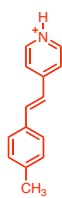
### Cation-π interaction



### Charge repulsion

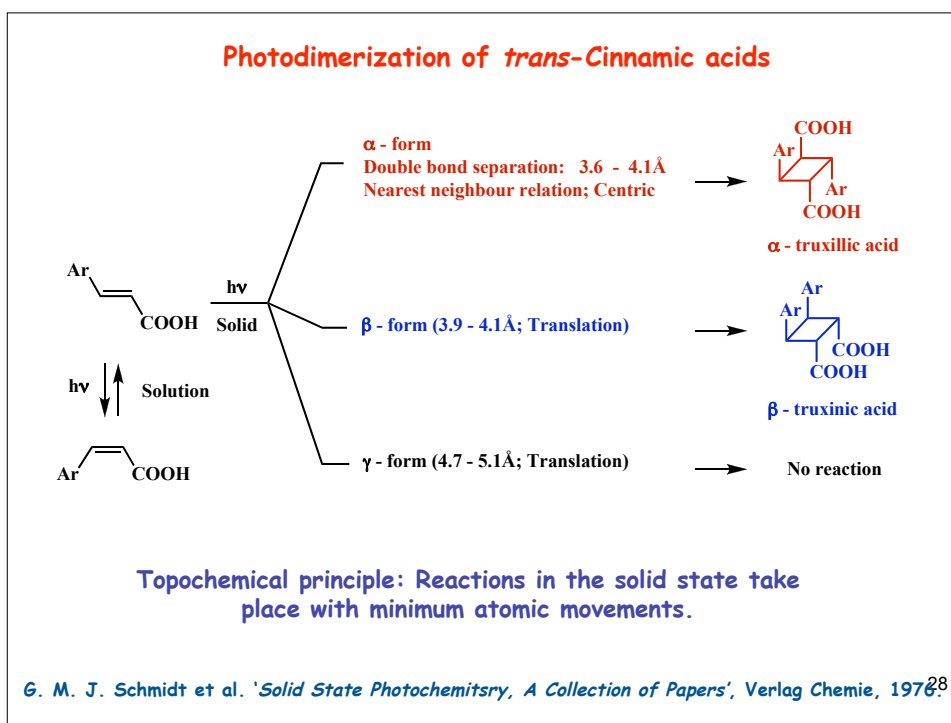
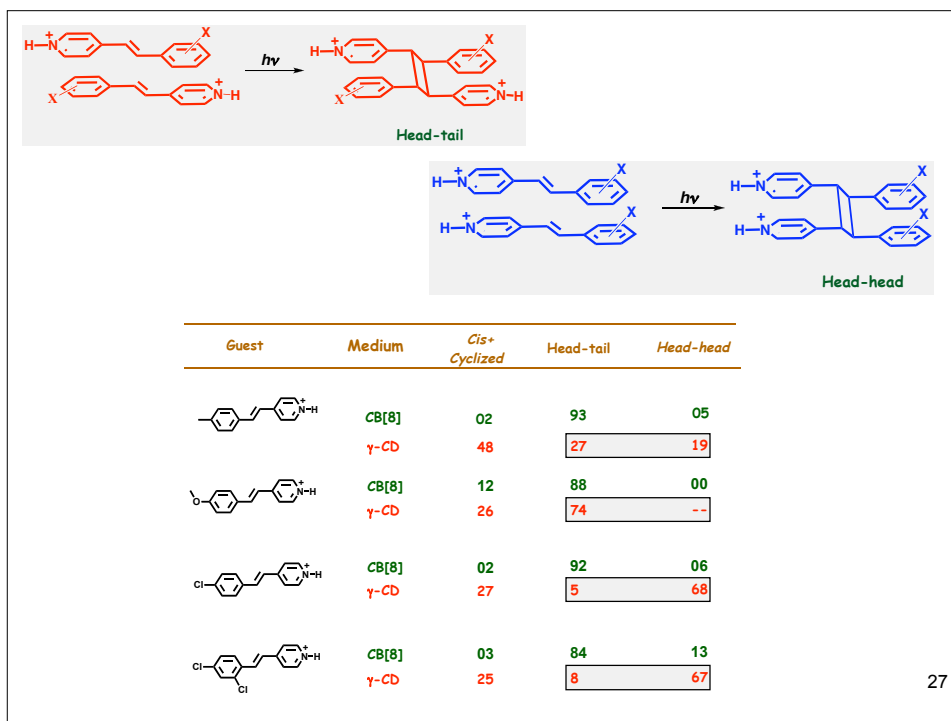


Can additional weak interactions (eg. Cl<sup>-</sup>...Cl) alter the olefin pre-orientation?

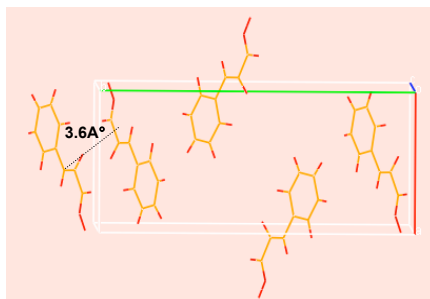


Counter anion Cl<sup>-</sup>

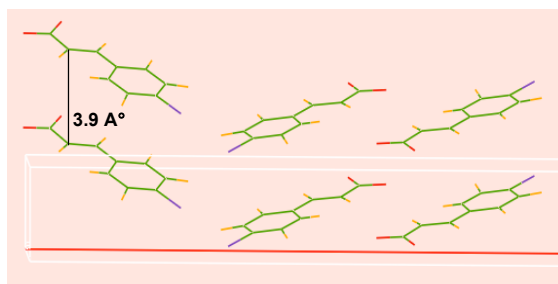
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$\alpha$ -*trans*-Cinnamic acid  
Leads to centrosymmetric dimer

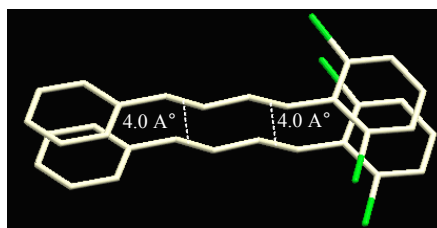
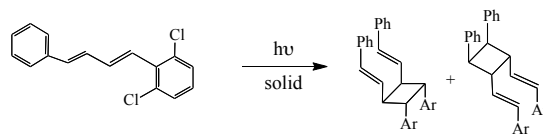
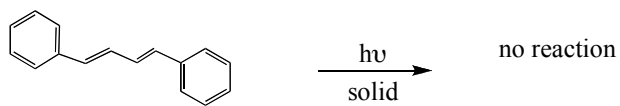


$\beta$ -*trans*-Cinnamic acid  
Leads to mirror symmetric dimer



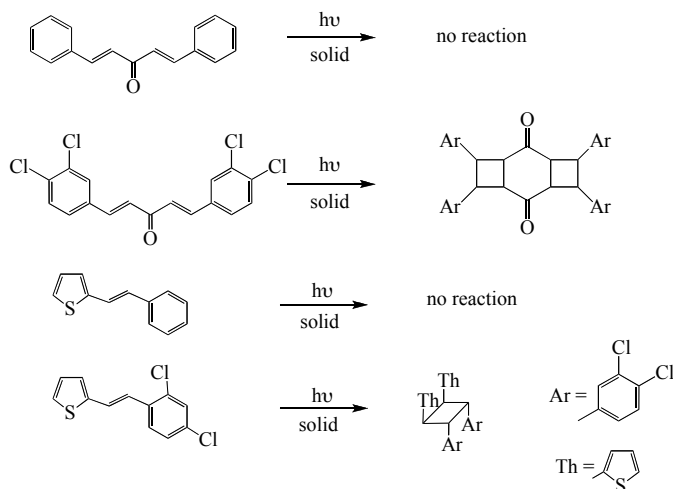
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### Templation through Cl---Cl interaction: Crystal engineering



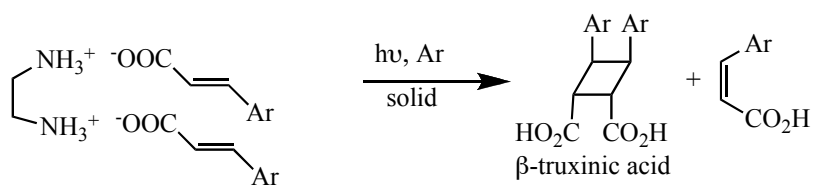
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## Templation through Cl---Cl interaction



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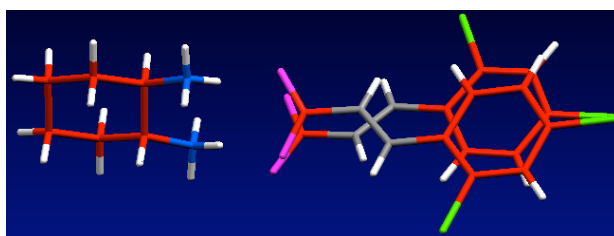
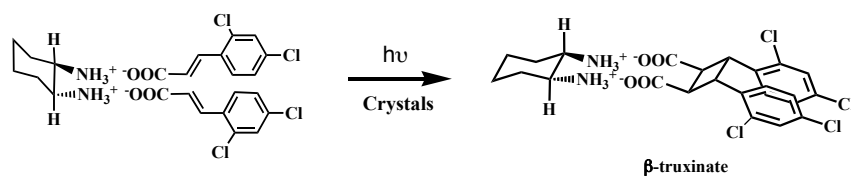
## Templation through ionic interaction



Ar = <i>o</i> -MeC <sub>6</sub> H <sub>4</sub>	30%	23%
Ar = <i>o</i> -ClC <sub>6</sub> H <sub>4</sub>	84	9
Ar = <i>m</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	70	4
Ar = 2-thienyl	13	0

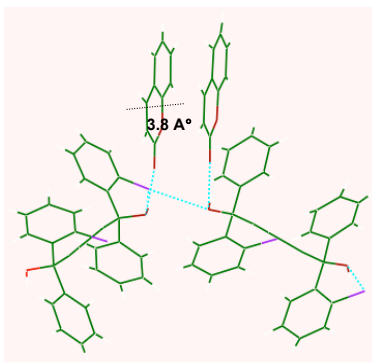
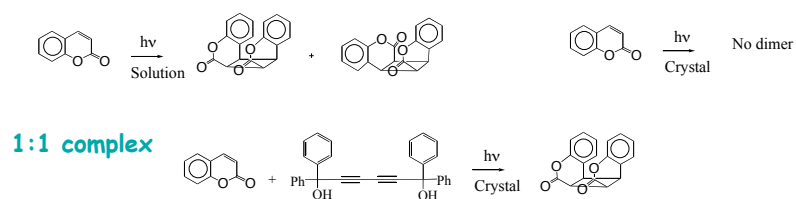


## Templation through ionic interaction



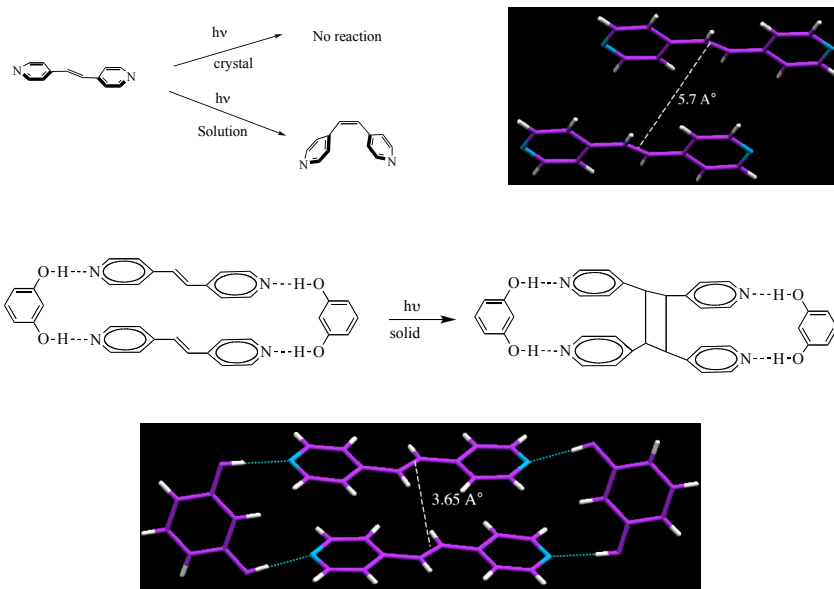
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## Templation through hydrogen bonding



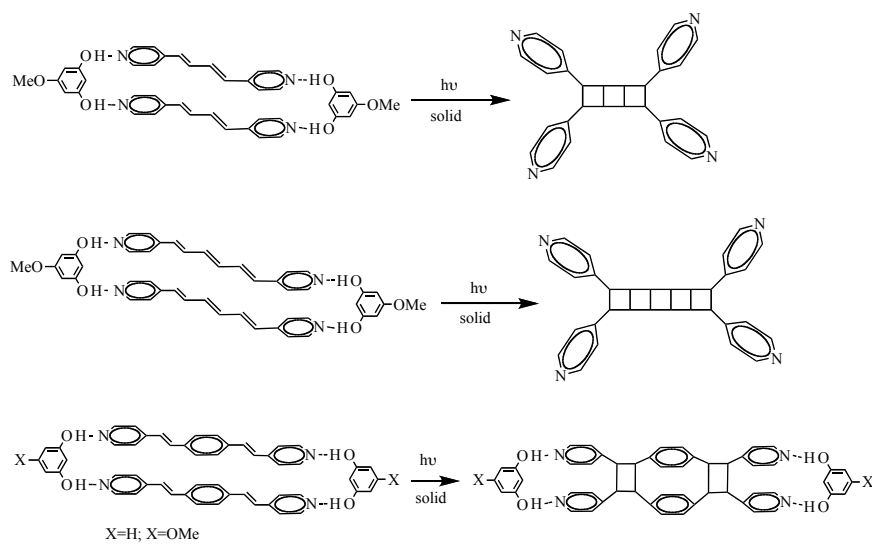
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## Templation through hydrogen bonding



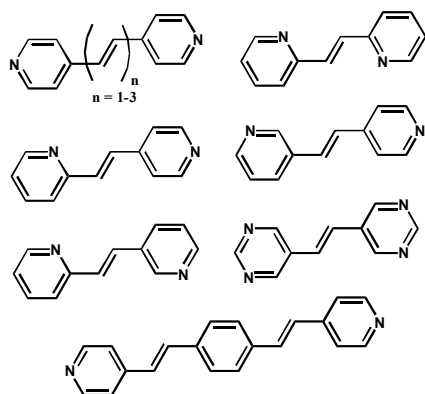
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## Templation through hydrogen bonding

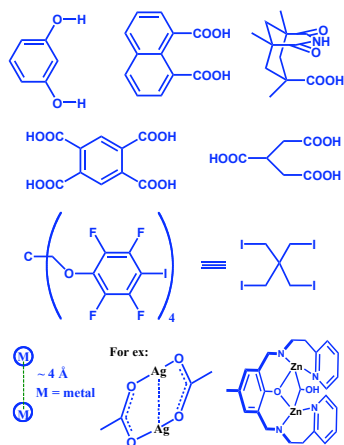


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## Single Template Does Not Work for Several Olefins



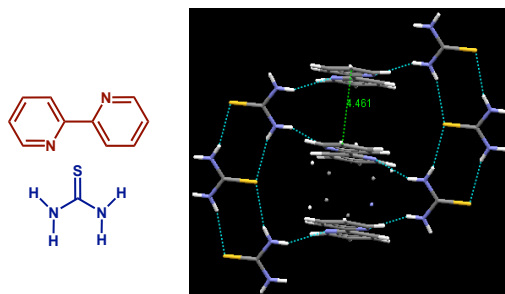
Reactive Olefins



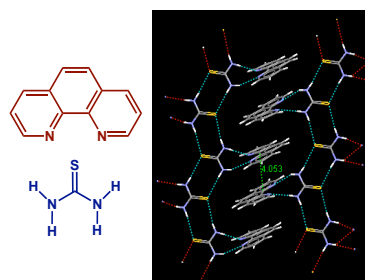
Templates

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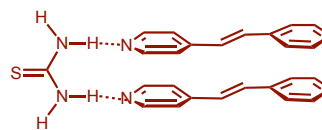
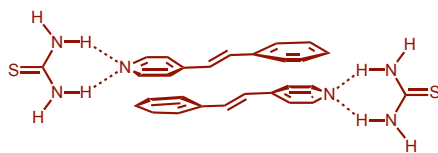
## Thiourea as a Template: Importance of Hydrogen Bonding



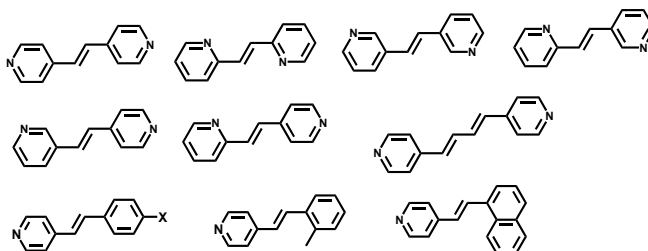
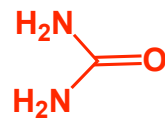
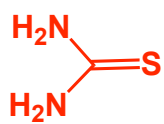
CSD entry: AMILIR



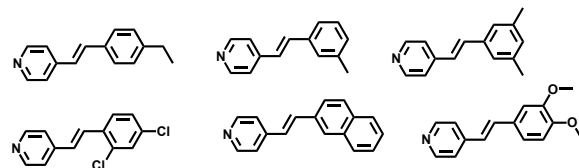
CSD entry: AMILOX



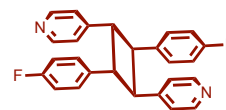
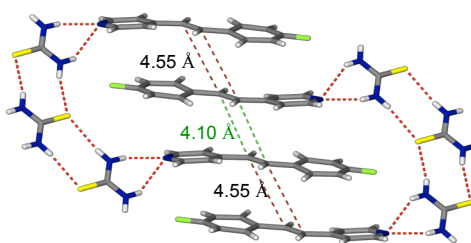
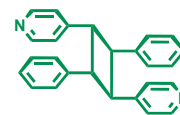
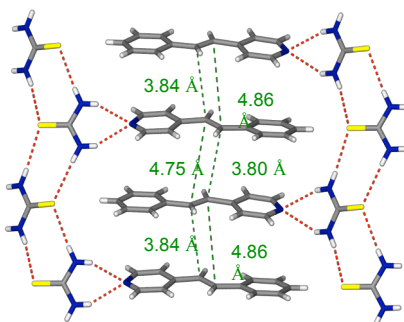
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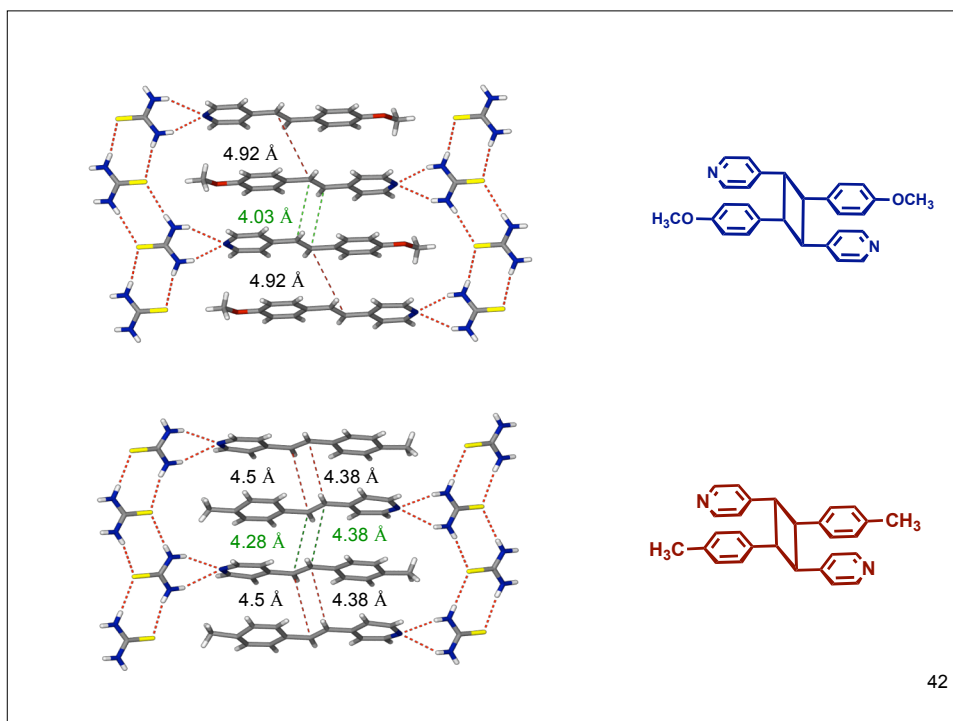
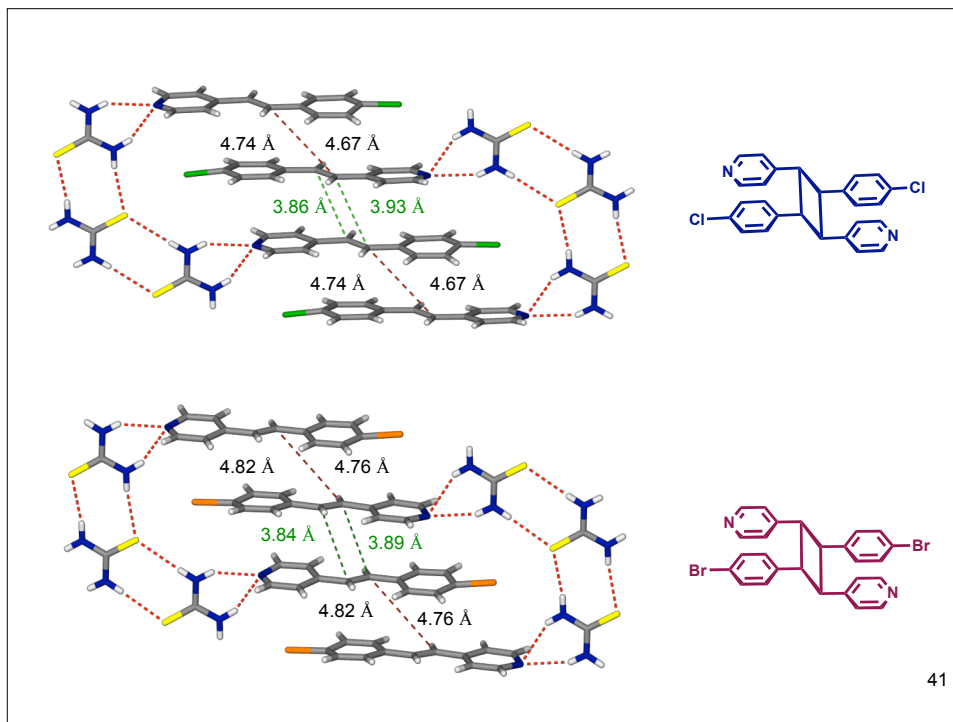
X = H, F, Cl, Br, Me, OMe and CN

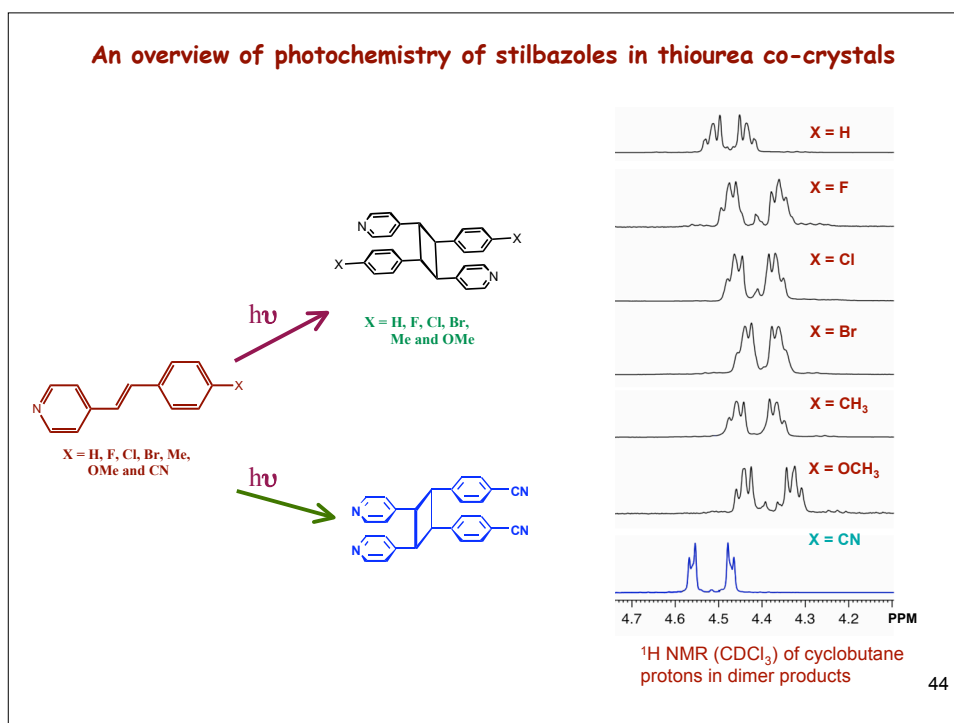
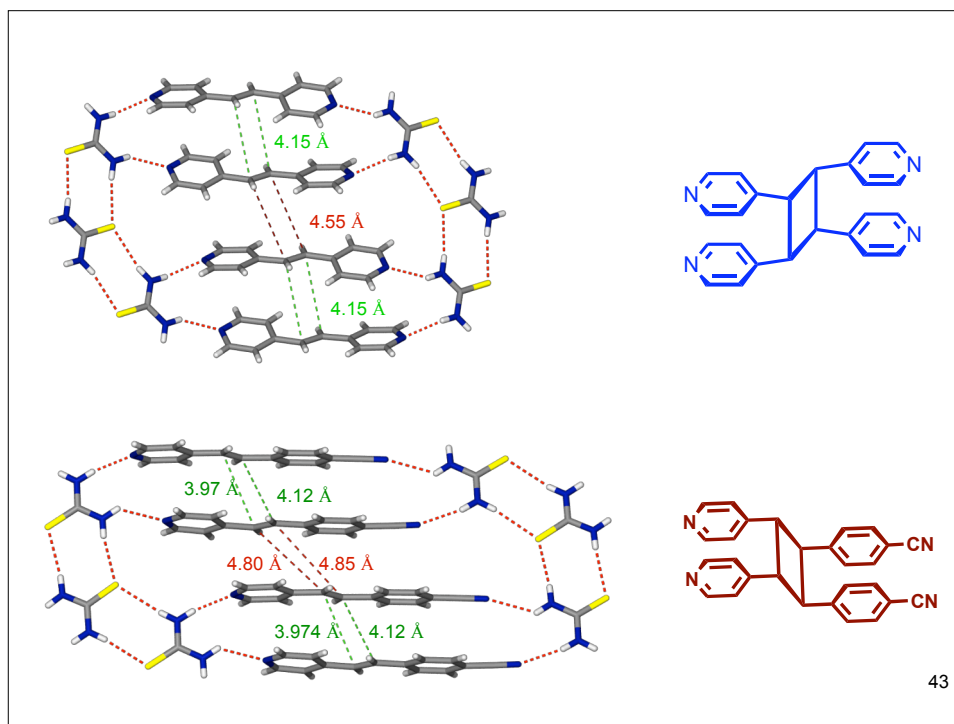


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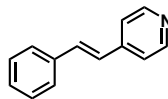
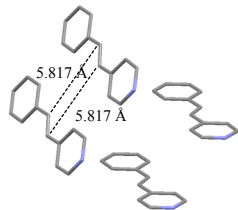


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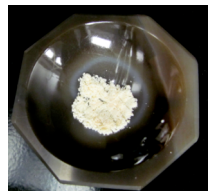




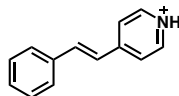
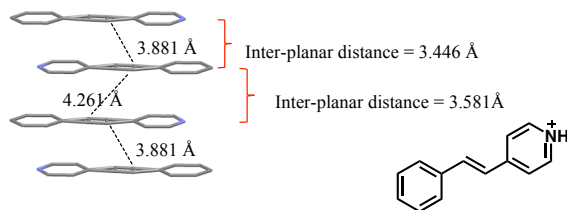
## Stilbazole not oriented suitably for photodimerization



### Stilbazole



E. Cariati, D. Roberto, R. Ugo, V. I. Srdanov, S. Galli, P. Macchi, A. Sironi *New J. Chem.* **2002**, *26*, 13.

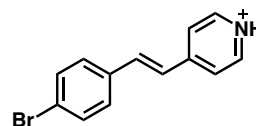
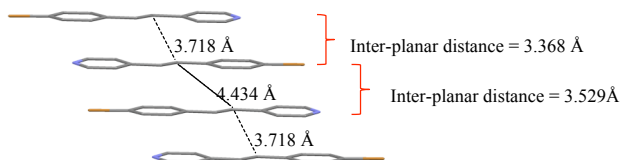
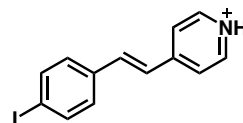
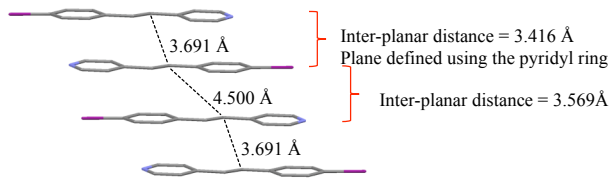


### Stilbazole + HCl



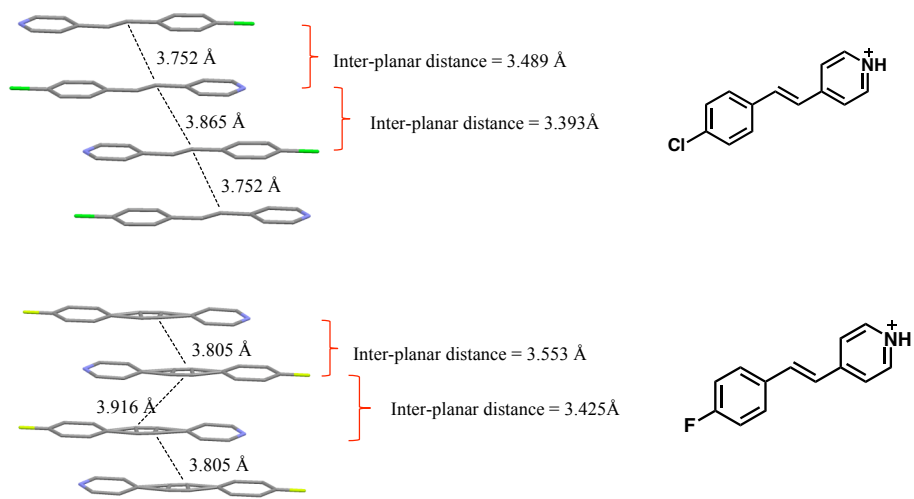
45

## 4-Halo Stilbazole.HCl Salt

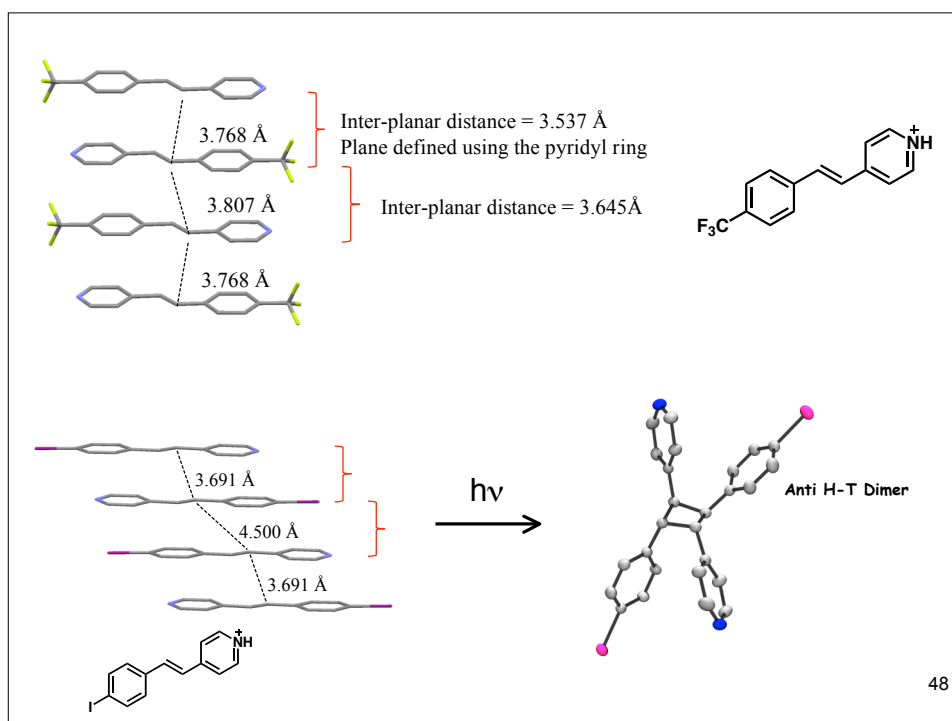


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## 4-Halo Stilbazole.HCl Salt



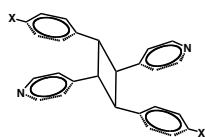
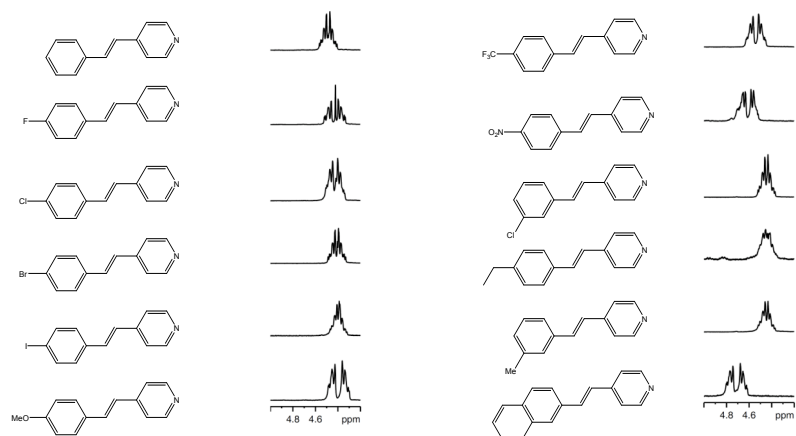
47



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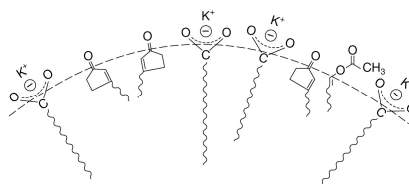
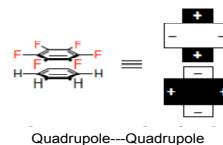
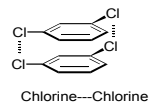
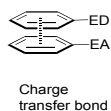
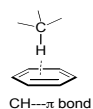
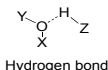
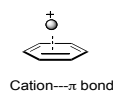
## Photodimerization of Stilbazole.HCl Salts



Anti H-T Dimer

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## Weak interactions help orient molecules



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