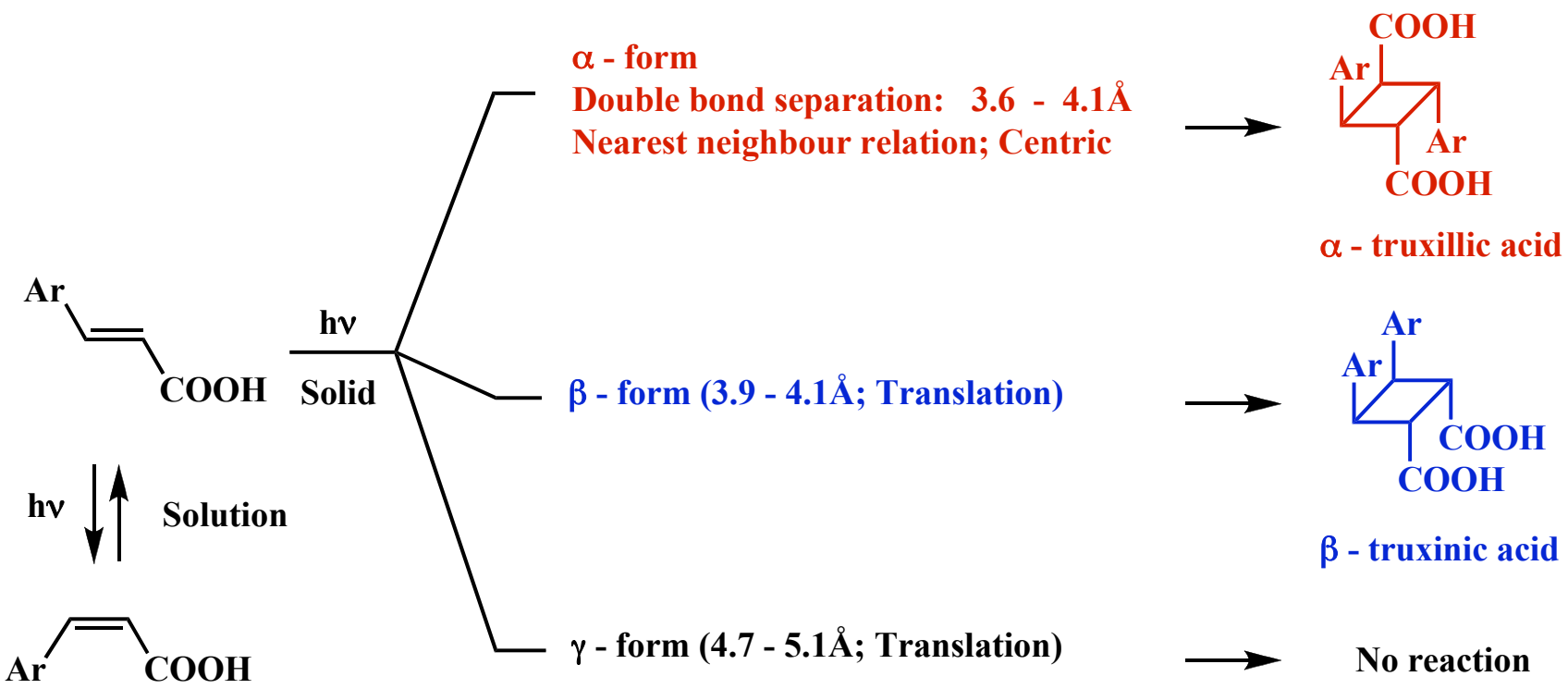
The Nobel Prize in Chemistry 1964
"for her determinations by X-ray techniques of the structures of important biochemical substances"

She belonged to many international peace organizations and, owing to Cold War restrictions, was not permitted to obtain a U.S. visa until 1990.

Photodimerization of *trans*-Cinnamic acids

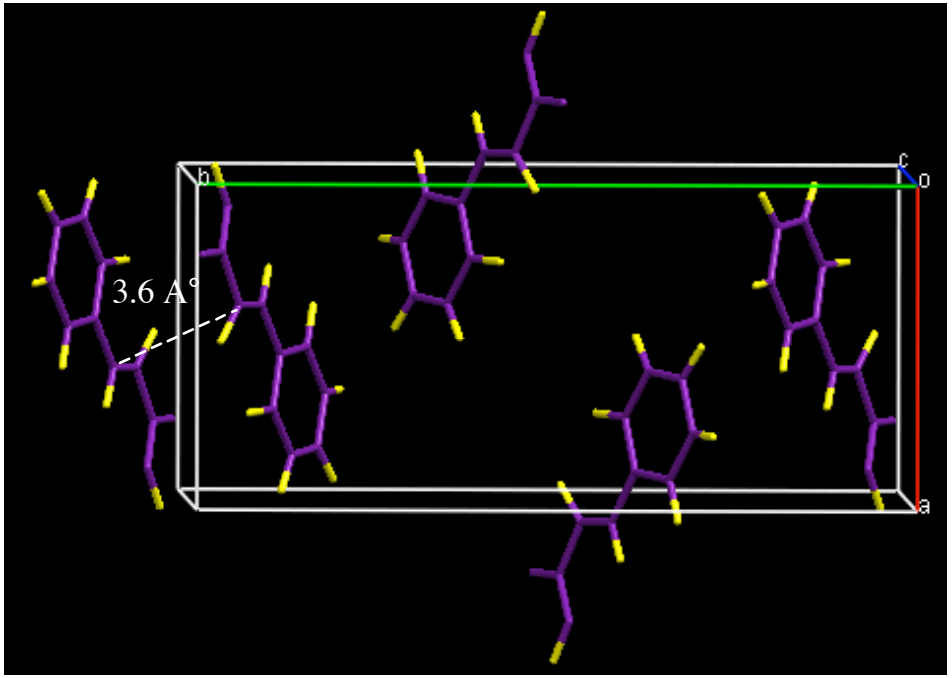


Topochemical principle: Reactions in the solid state take place with minimum atomic movements.

G. M. J. Schmidt et al. '*Solid State Photochemitsry, A Collection of Papers*', Verlag Chemie, 1976.

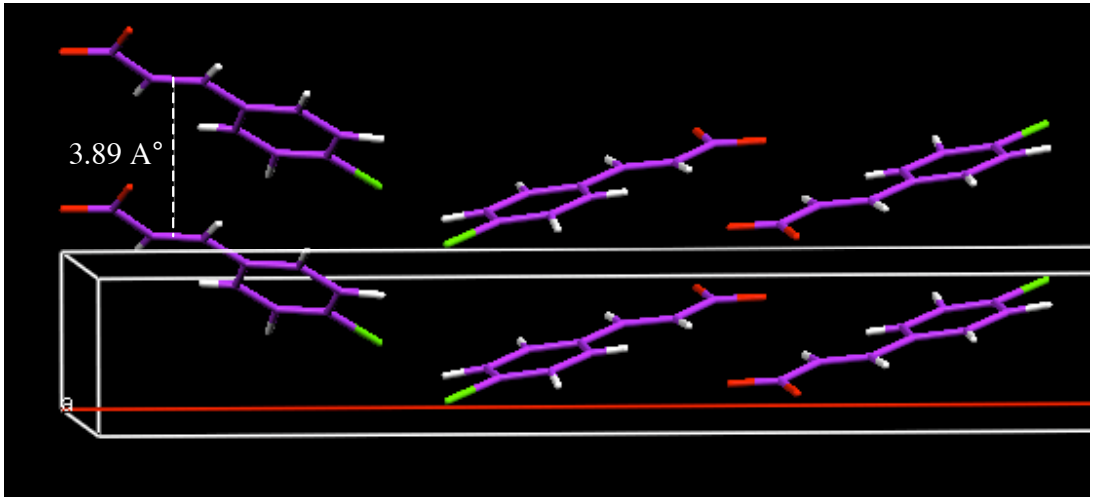
α-*trans*-Cinnamic acid

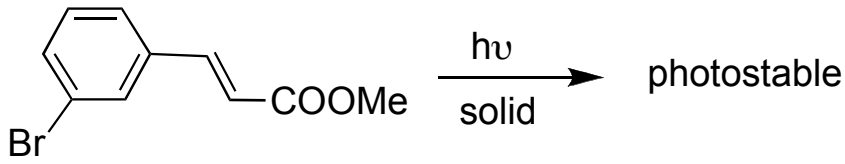
Leads to centrosymmetric dimer

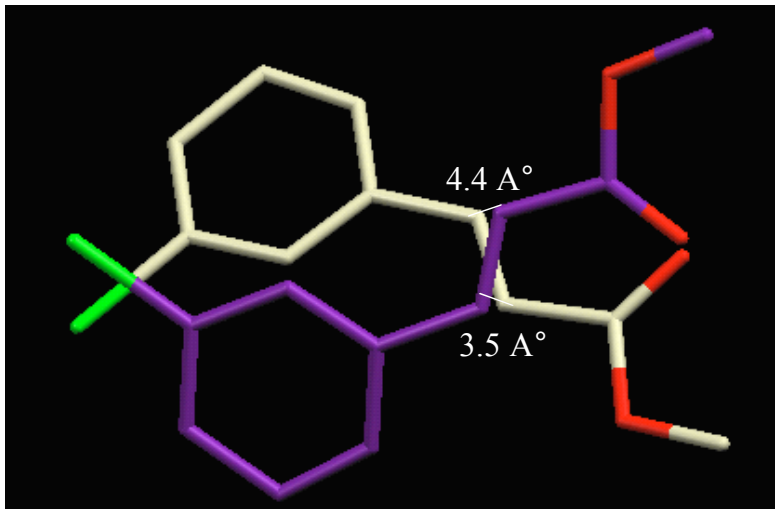


β-*trans*-Cinnamic acid

Leads to mirror symmetric dimer







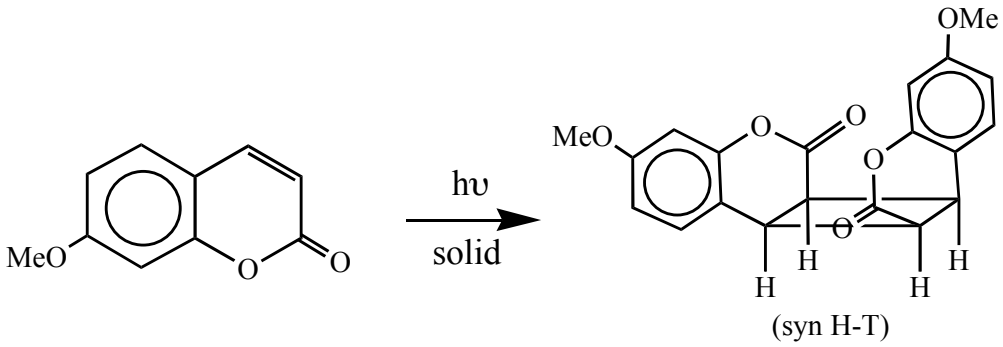
Packing arrangement of methyl-*meta*-bromocinnamate.

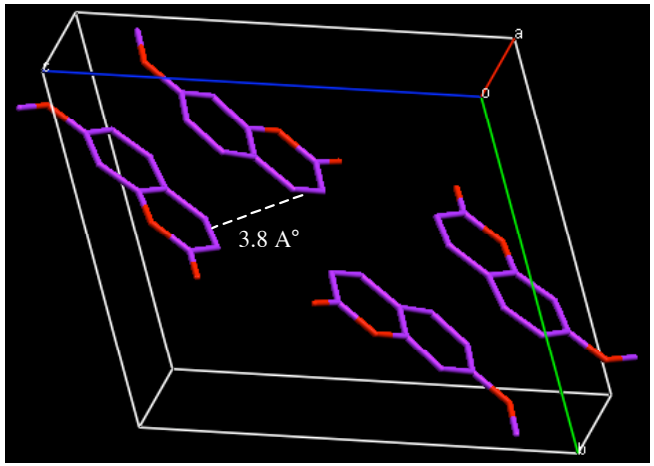
Note that the two reactive double bonds are not parallel to one another.

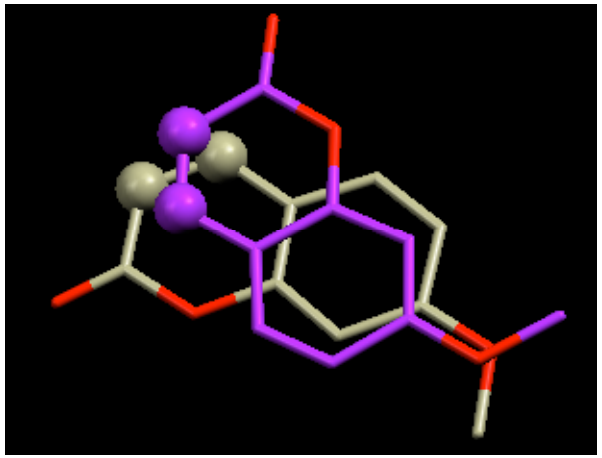
Topochemical principle: Reactions in the solid state take place with minimum atomic movements.

Crystal Engineering

G. M. J. Schmidt et al. '*Solid State Photochemitsry, A Collection of Papers*', Verlag Chemie, 1976.





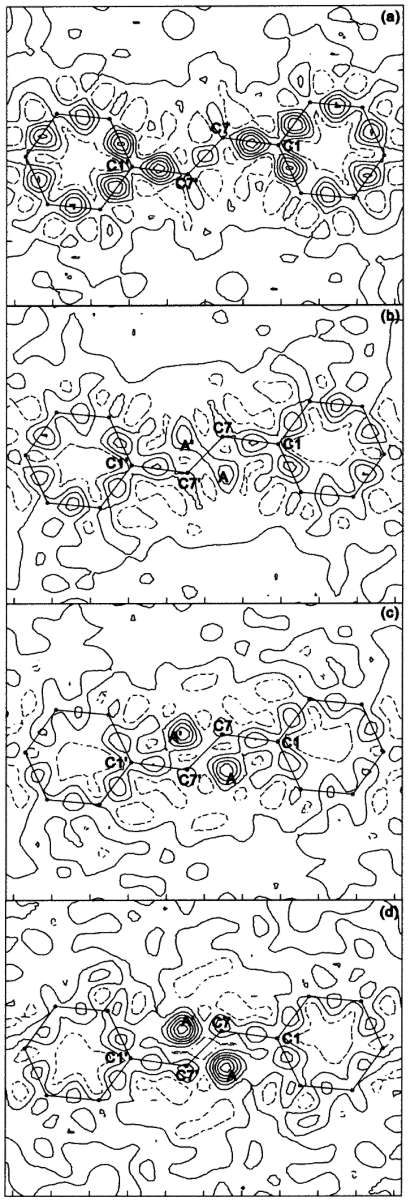


K. Venkatesan, V. Ramamurthy et. al., (1984)

The next decade will surely see more use of crystallographic information in the field of large-amplitude molecular motions in the solid state

J. D. Dunitz, V. Schomaker and K. N. Trueblood (1988)

Difference Fourier maps of (*E*)-stilbene



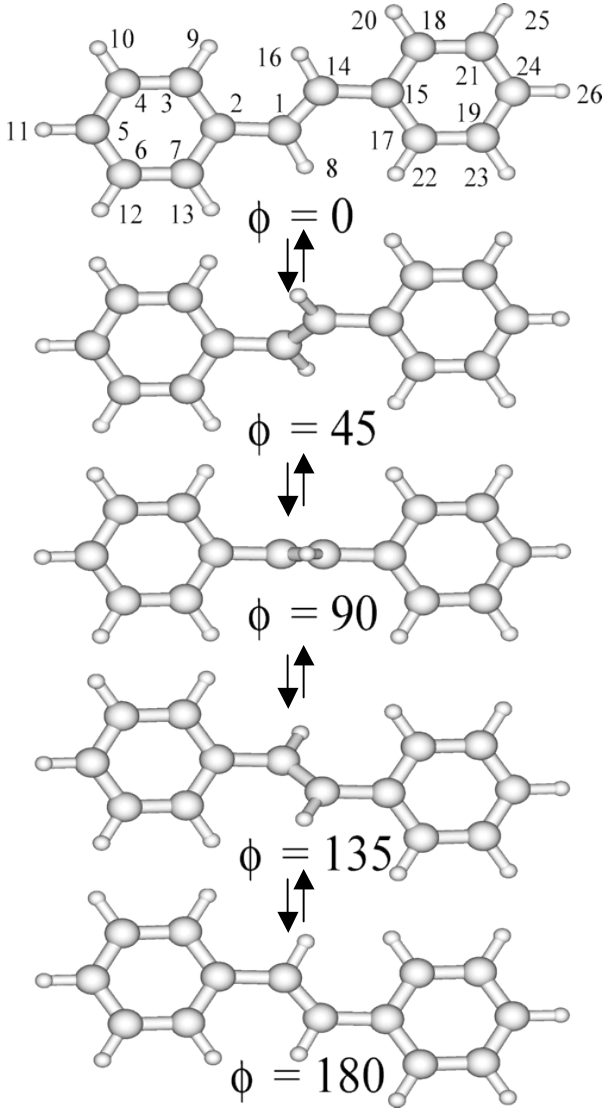
at 150 K

at 300

at 340

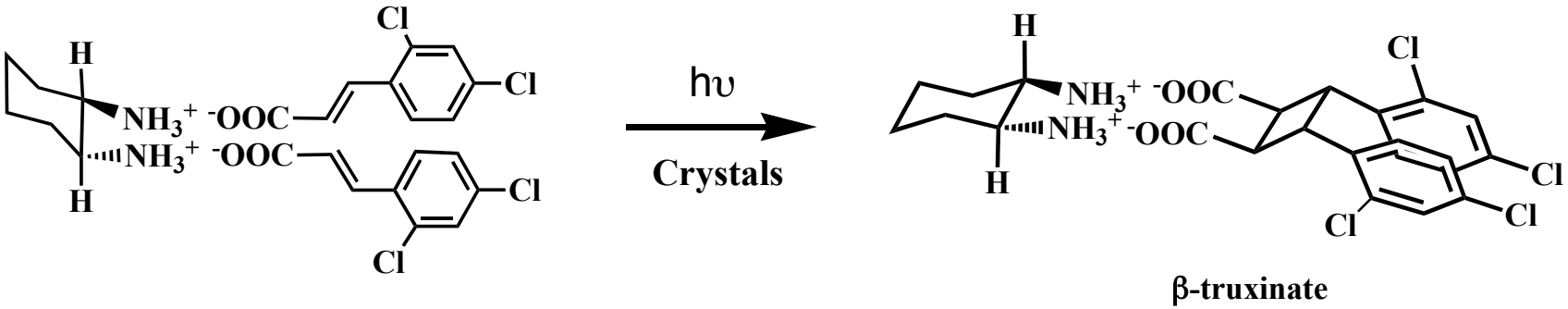
at 373

Pedal motion of stilbenes



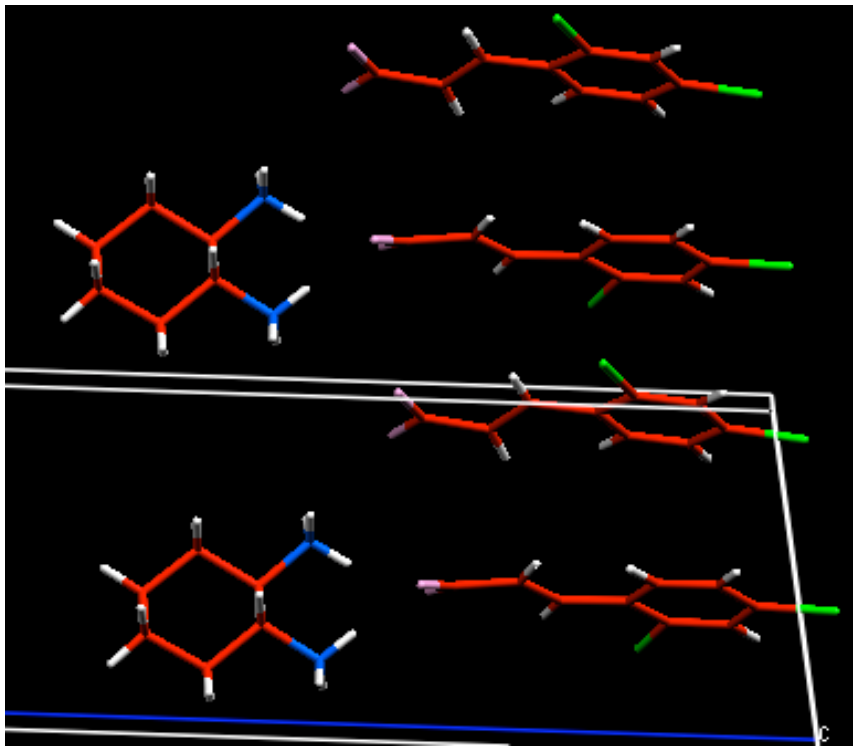
Harada and Ogawa, JACS, 126, 3539 (2004).

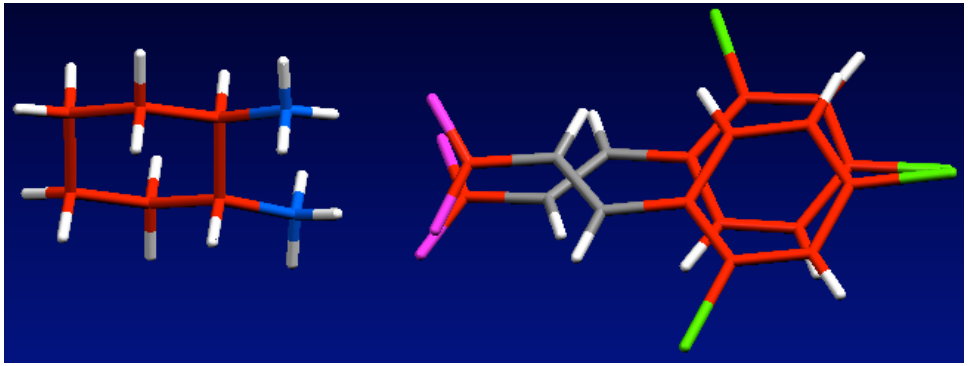
Photodimerization of criss-cross alkenes



β-truxinate

Time of hυ (hrs)	% conv.	β-truxinate	cis	δ-dimer
7	23	20	3	trace
12	35	30	4	1
21	45	38	5	2
32	57	49	6	2

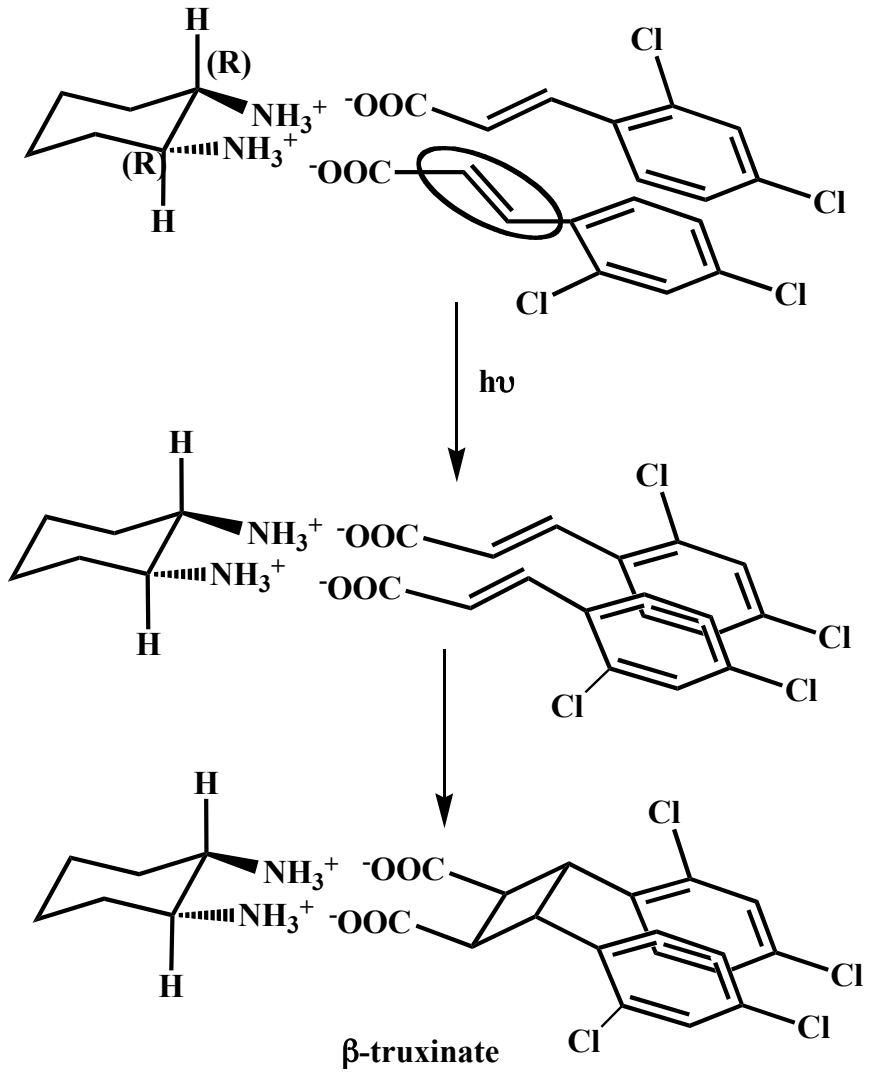




d_1 = 3.9 A° and d_2 = 4.1 A°

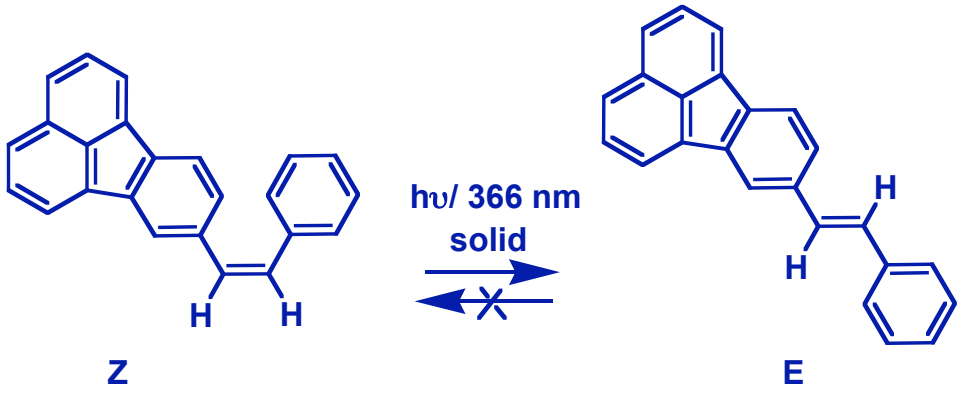
Large motions are tolerated in the crystal

- *C=C* exists in criss-crossed arrangement.
- Pedal-like conformational change by one of the cinnamic acid molecules is required for β-dimer formation.

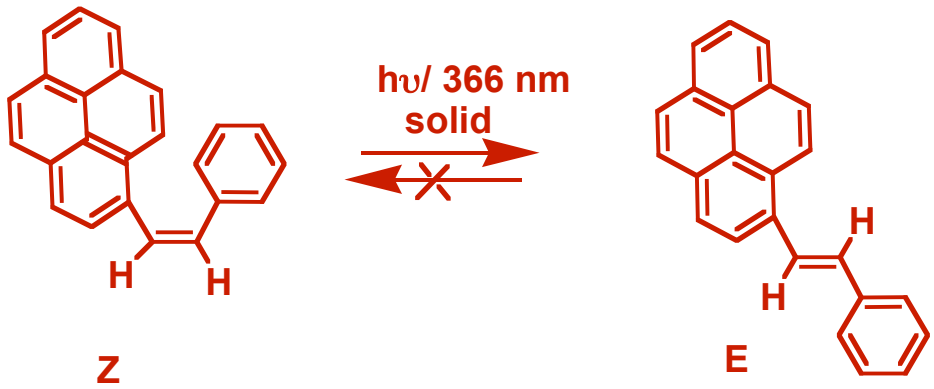


Cis-Trans Photoisomerization in Crystals

Temp °C	Duration	%Conversion
RT	12	100
50°C	6	100



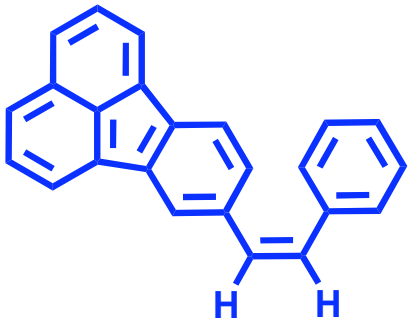
Temp °C	Duration	%Conversion
RT	12	15
50°C	18	60



Temp °C	Duration	%Conversion
RT	45	80
50°C	21	100

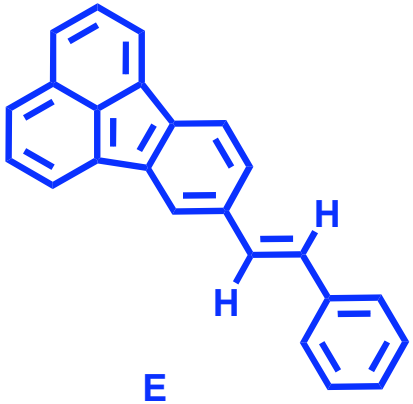
T. Arai

Photoisomerization of *cis*-8-fluoranthenyl styrene

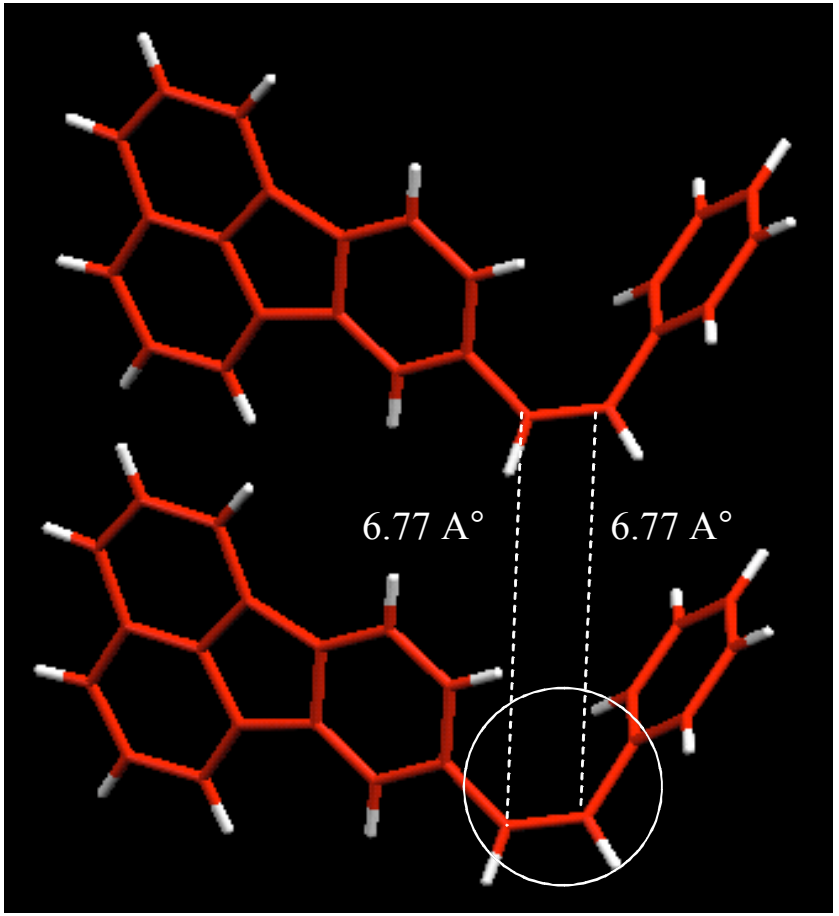


Z

hυ/ 366 nm

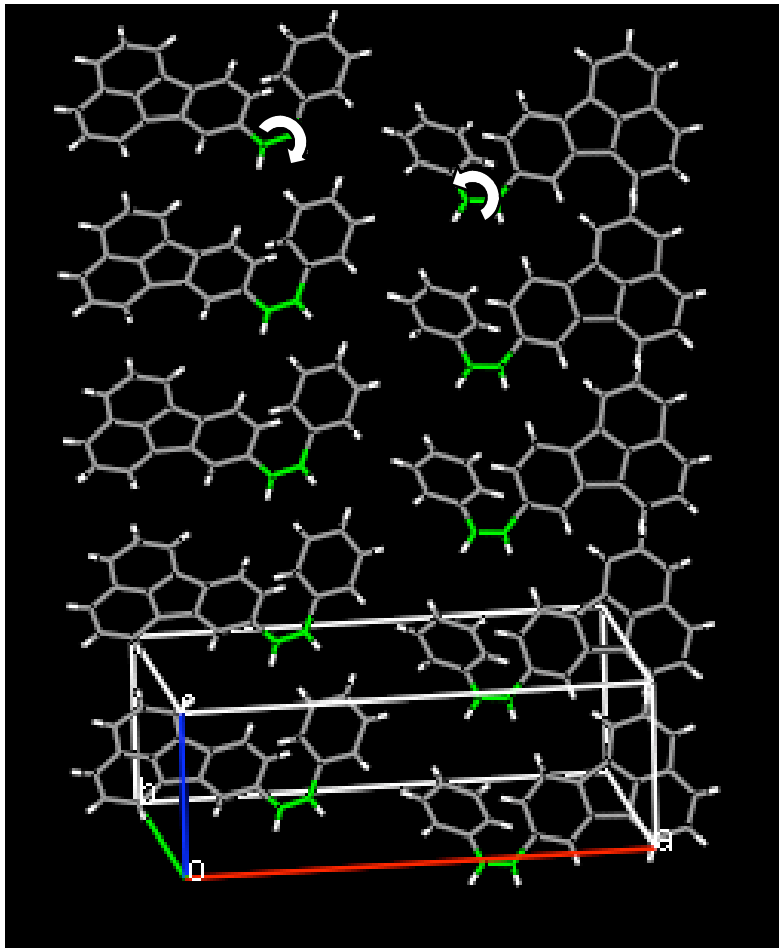


E

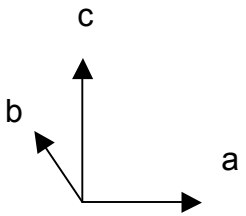


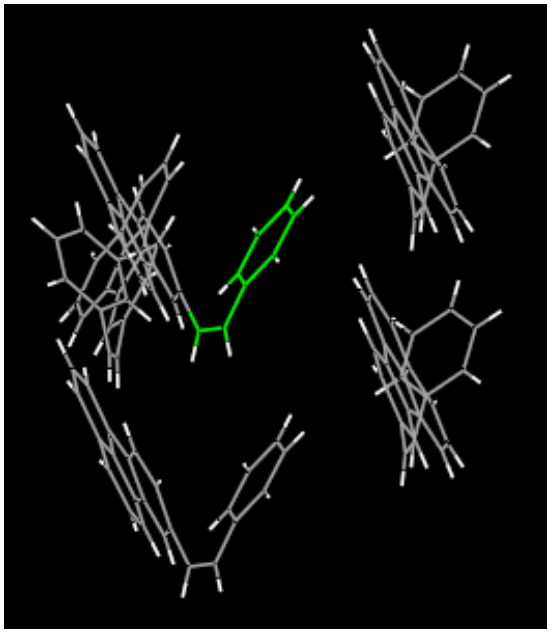
Large distance between the reactive double bonds 6.77 A° precludes cyclobutane intermediate.

Photoisomerization of *cis*-8-fluoranthenyl styrene



Empty channel along *c* axis

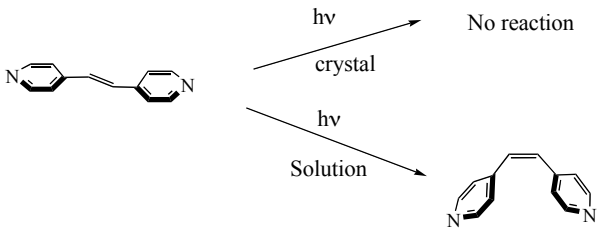




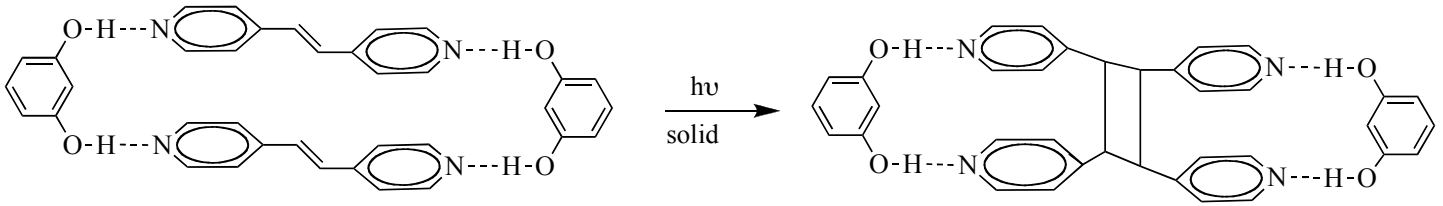
Absence of short contacts near reaction site favors rotation.

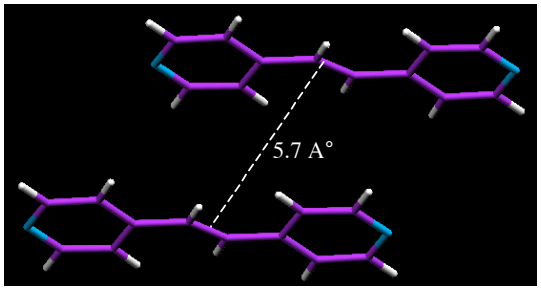
C---C > 3.4 A°
C---H > 2.8 A°
H---H > 2.4 A°

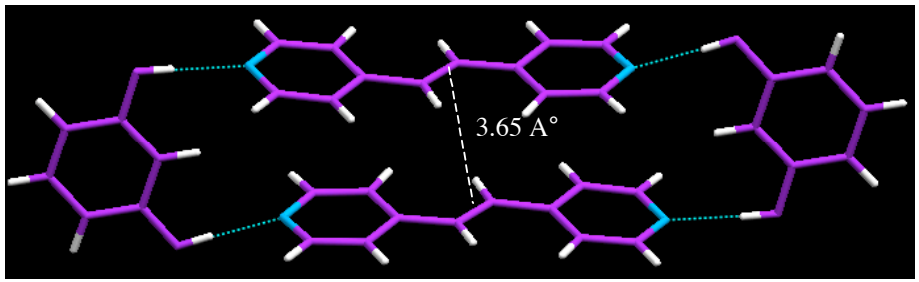
Pre-organization with a guest: Non reactive molecule made to react



In solution isomerization
In crystals no reaction

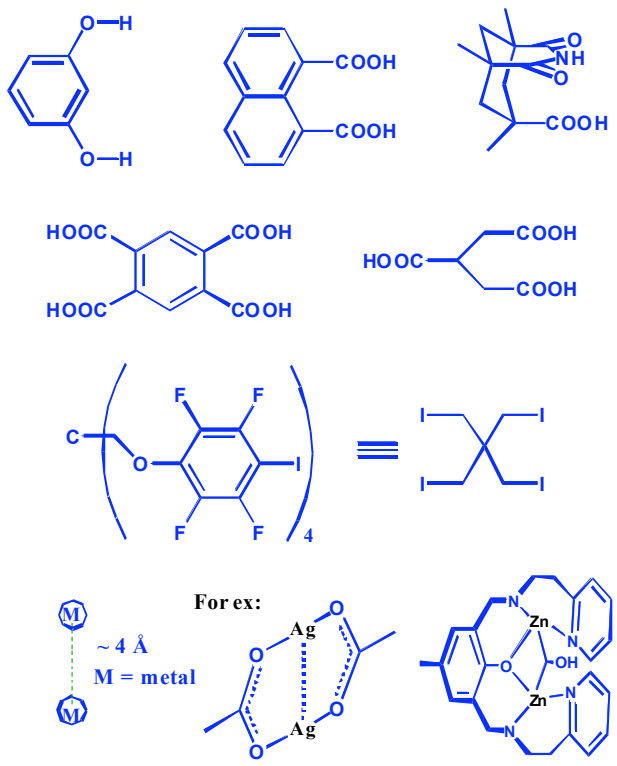


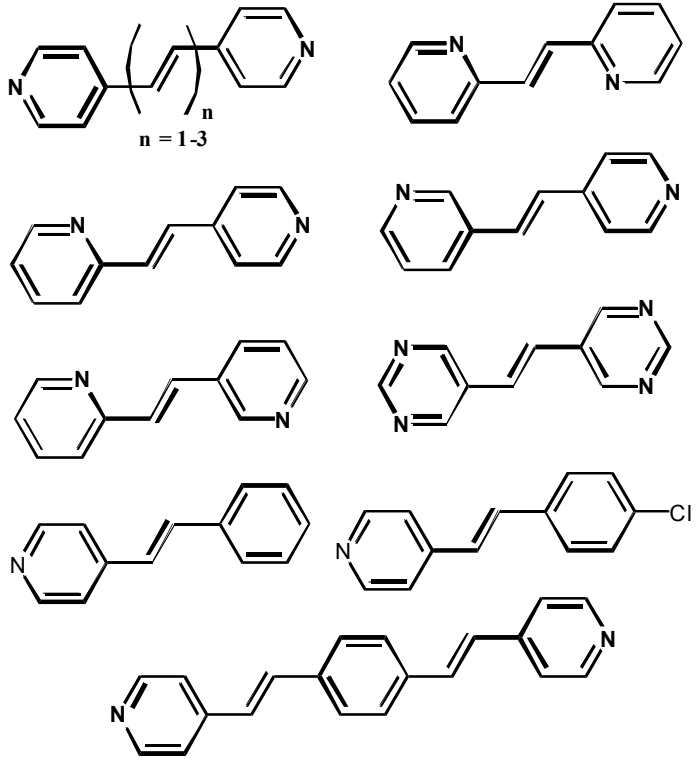




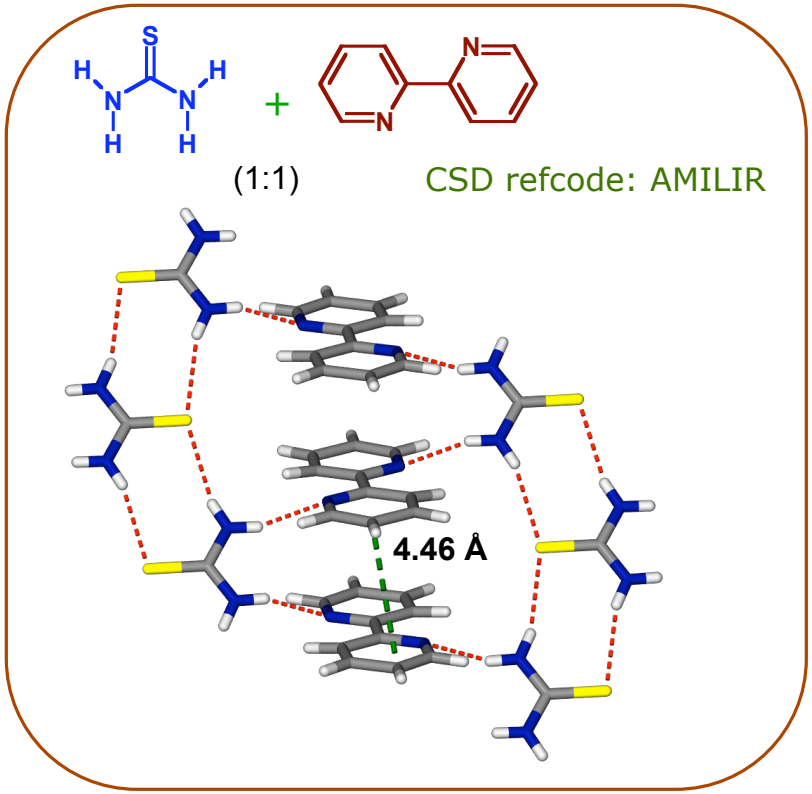
MacGillivray et. al., JACS, 2000, *122*, 7817.

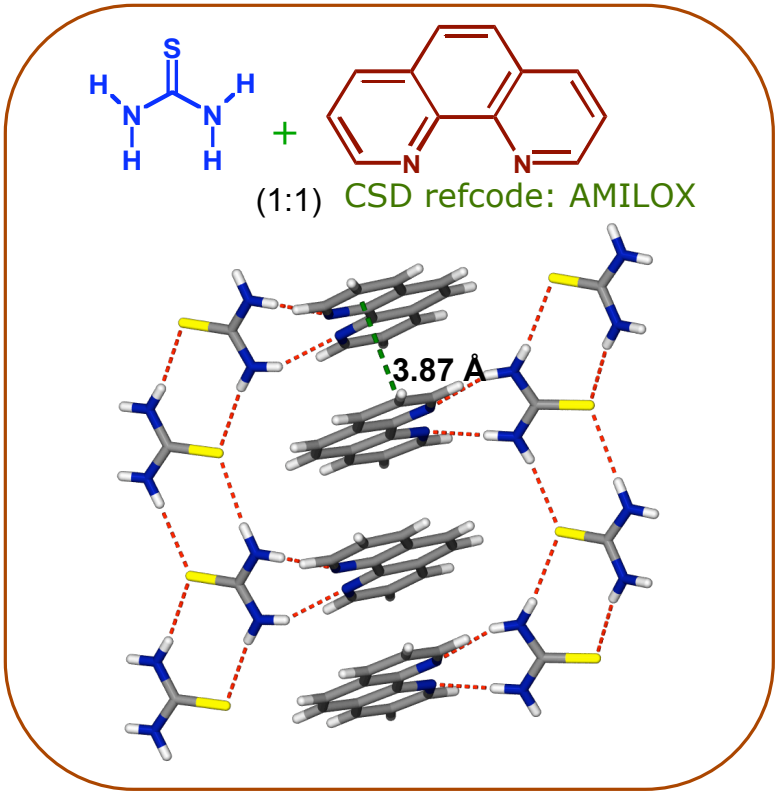
Overview of templated dimerization of olefins in solid-state

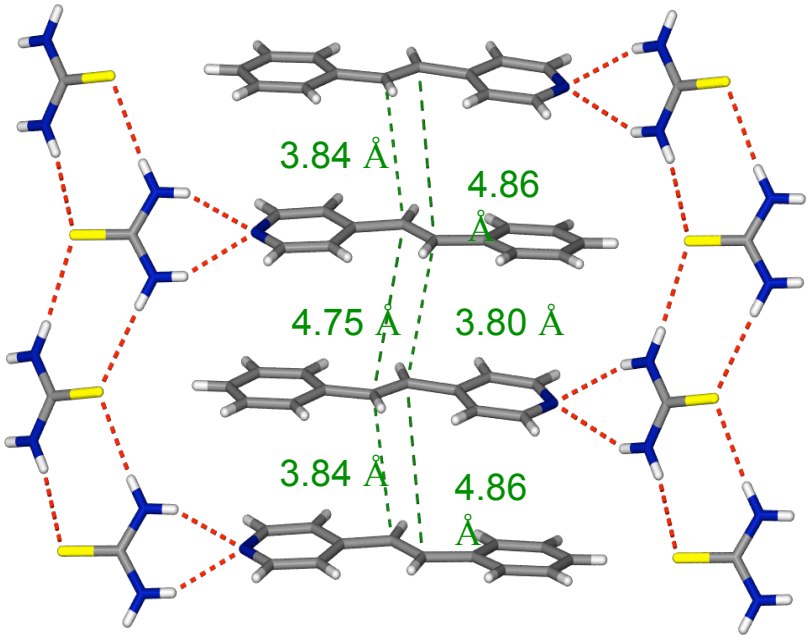




Thiourea as a possible template (Cambridge Structural Database)



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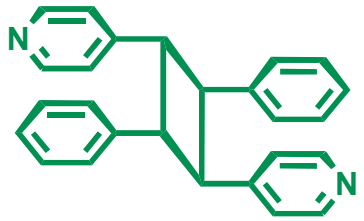
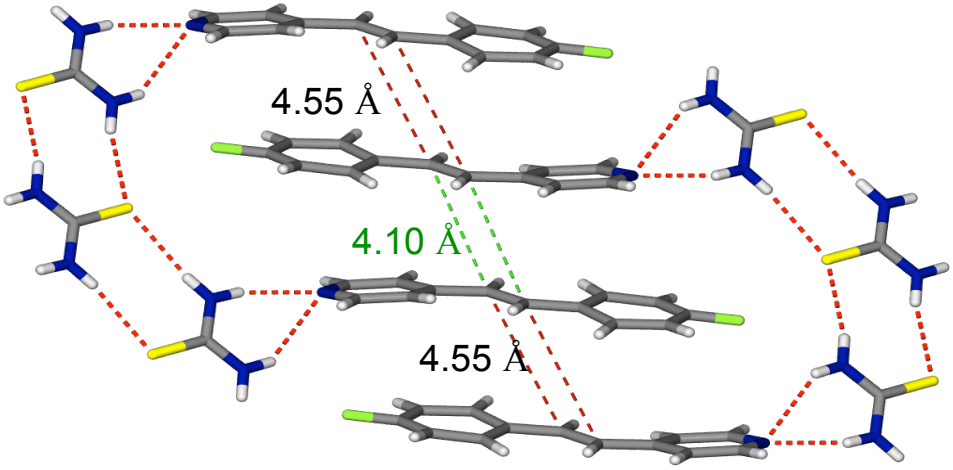
4.86 Å
4.75 Å
3.80 Å
3.84 Å
4.86 Å


N
N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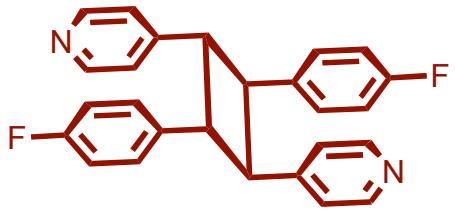
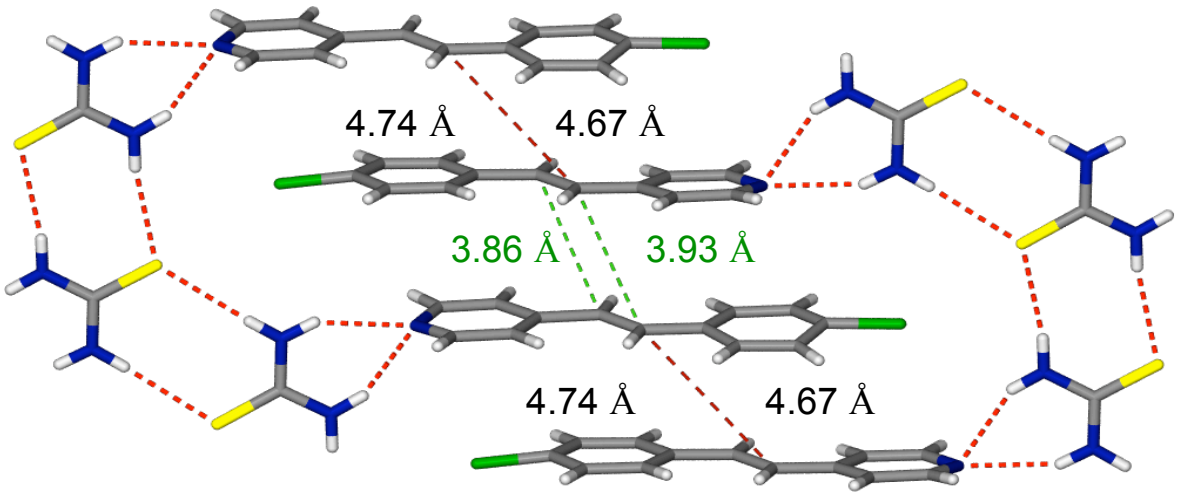
4.10 Å
4.55 Å


N
F
F
N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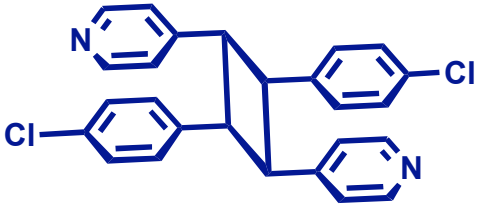
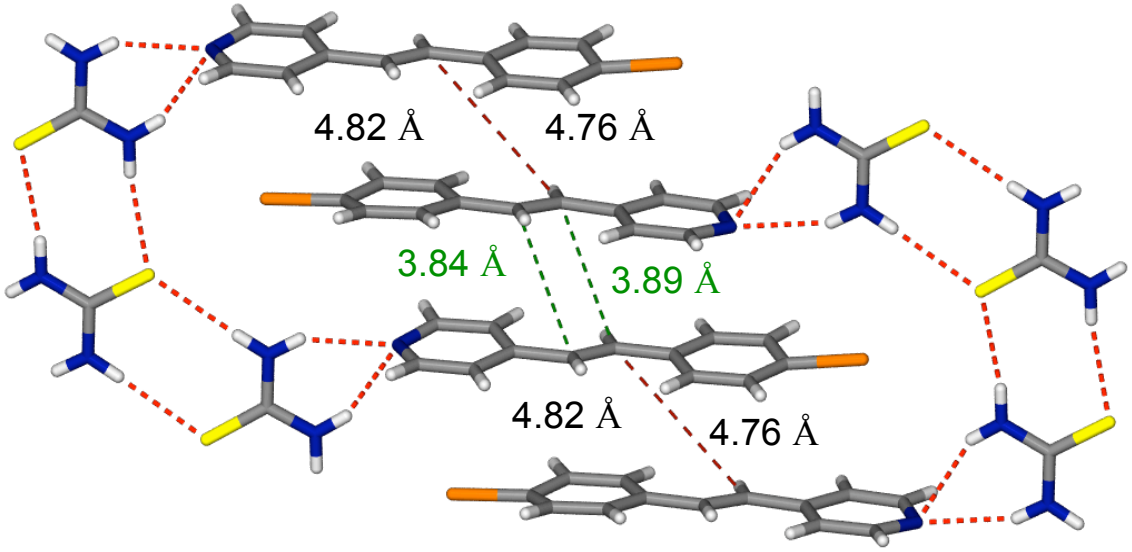
3.86 Å
3.93 Å
4.74 Å
4.67 Å


N
Cl
Cl
N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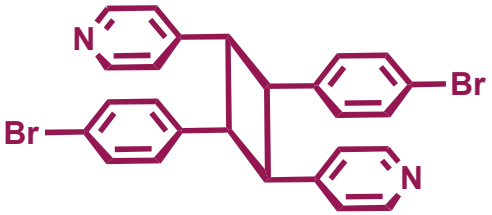
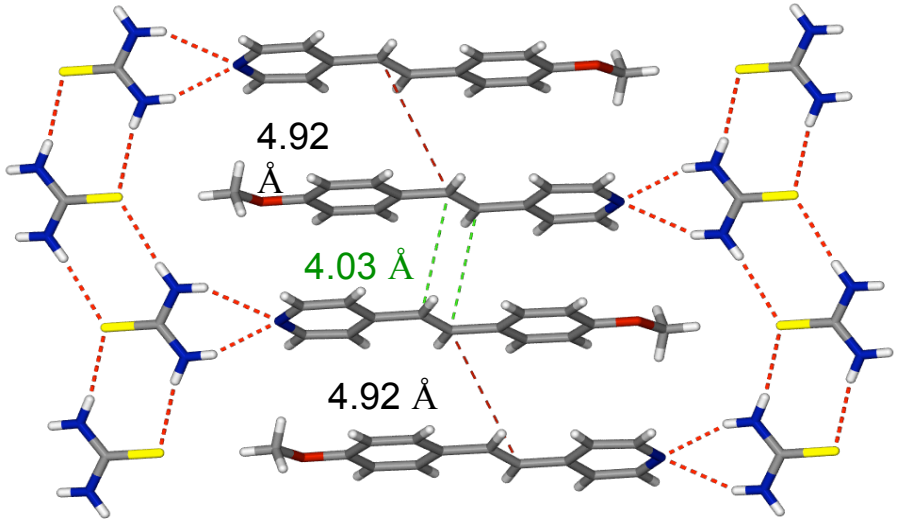
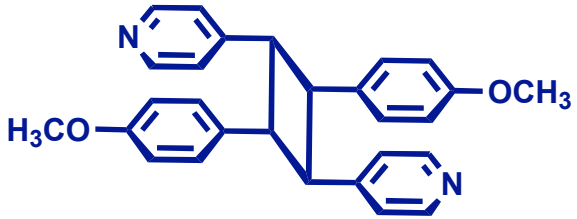
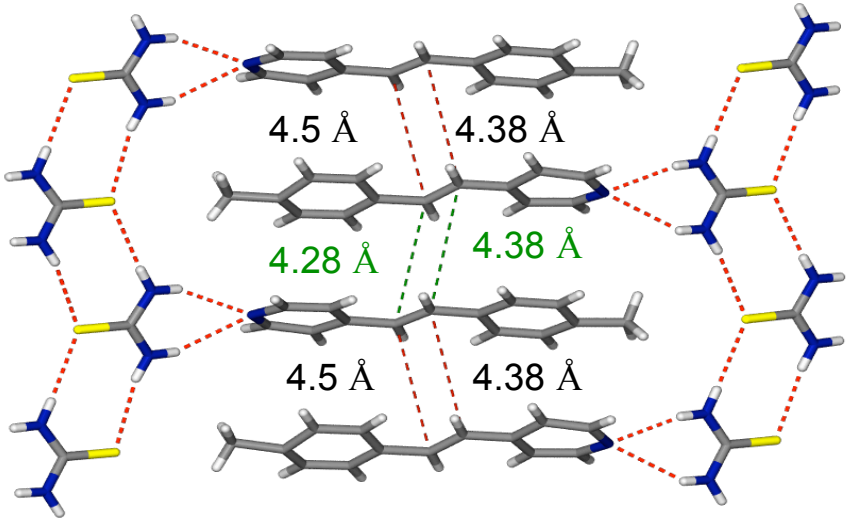
4.76 Å
3.84 Å
3.89 Å
4.82 Å
4.76 Å


N
Br
Br
N


4.92
Å
4.03 Å
4.92 Å


N
OCH3
H3CO
N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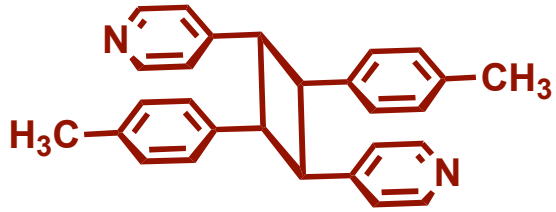
4.28 Å
4.38 Å
4.5 Å
4.38 Å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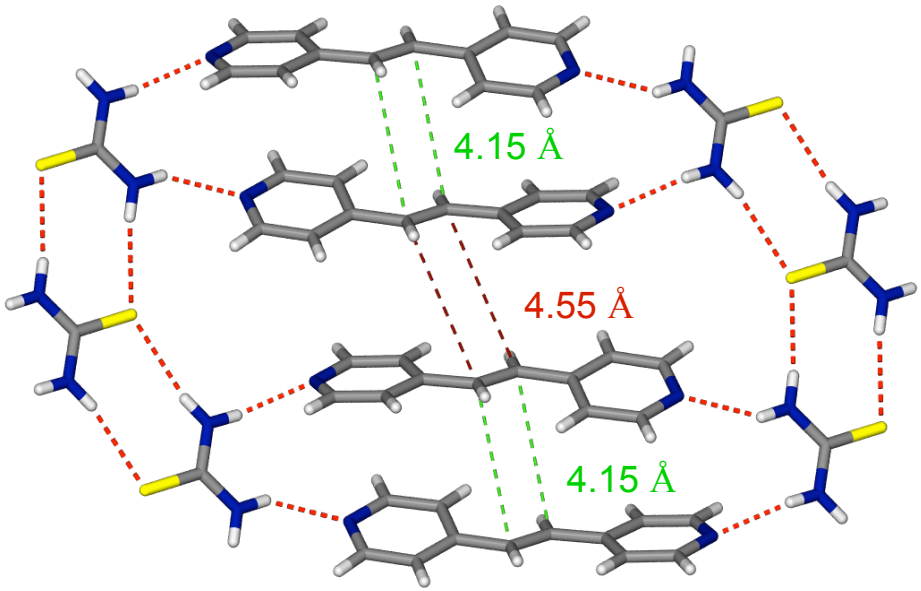
CH3
H3C
N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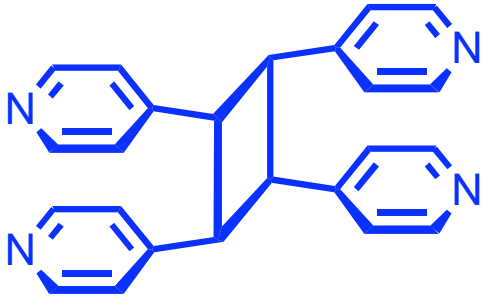
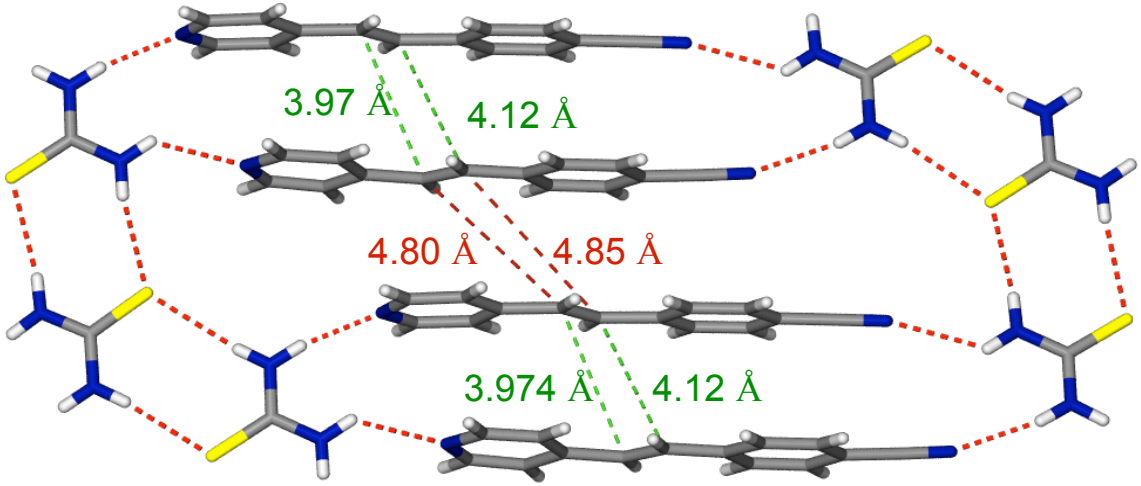
4.15 Å


N
N
N
N


3.97 Å
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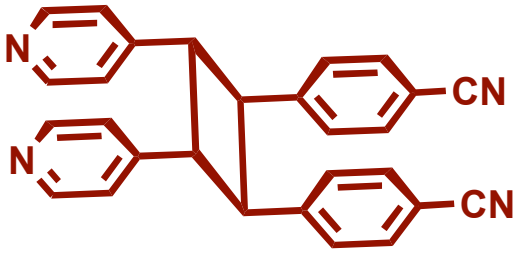
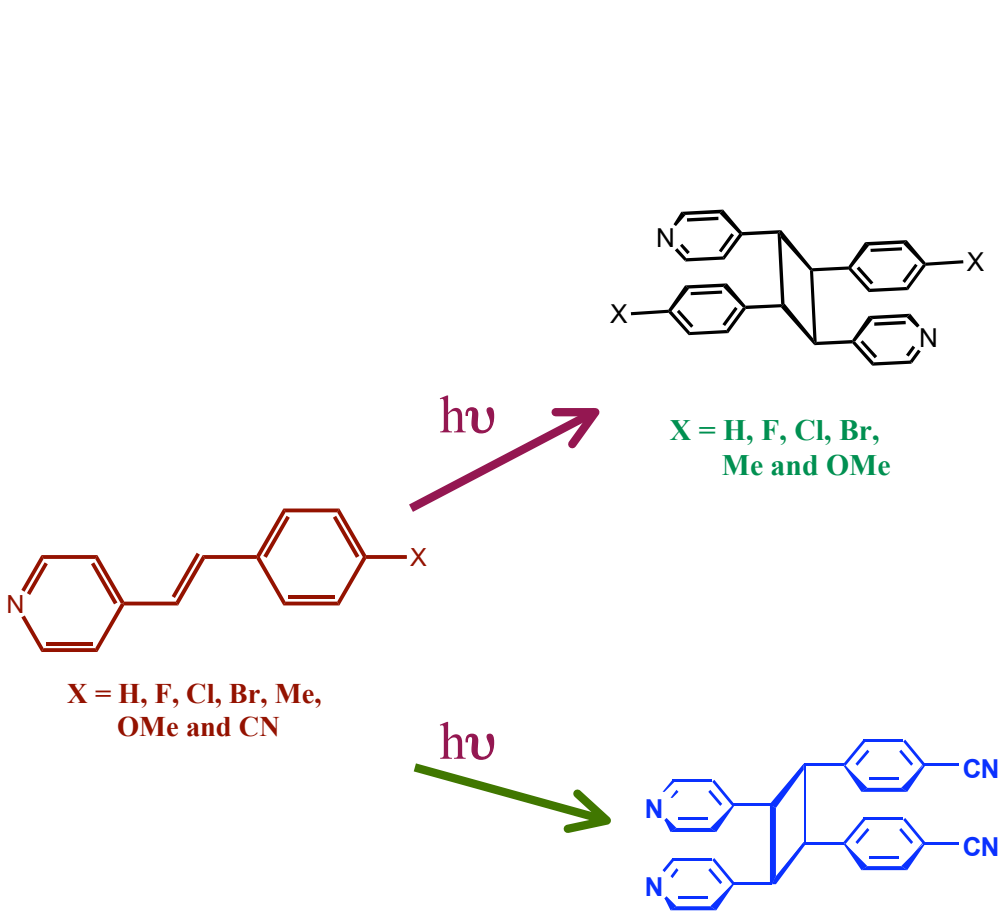
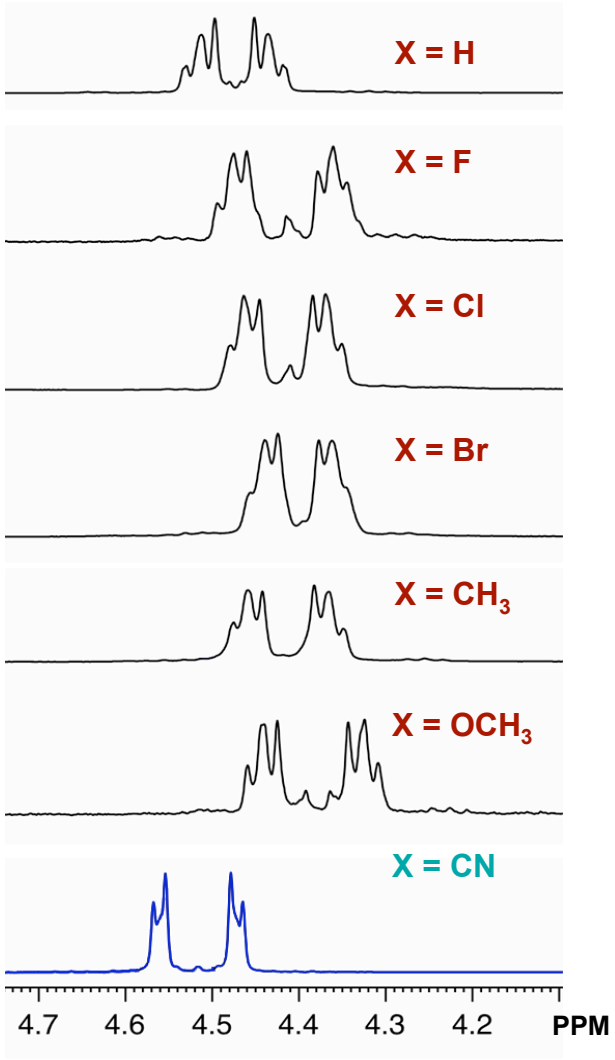
4.80 Å
4.85 Å
3.974 Å
4.12 Å


N
N
CN
CN

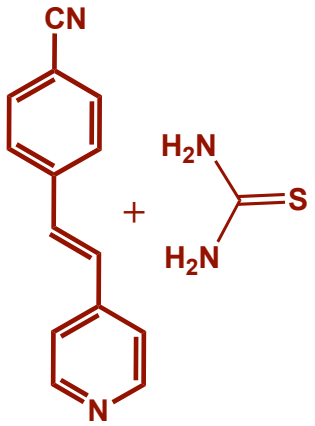
An overview of photochemistry of stilbazoles in thiourea co-crystals

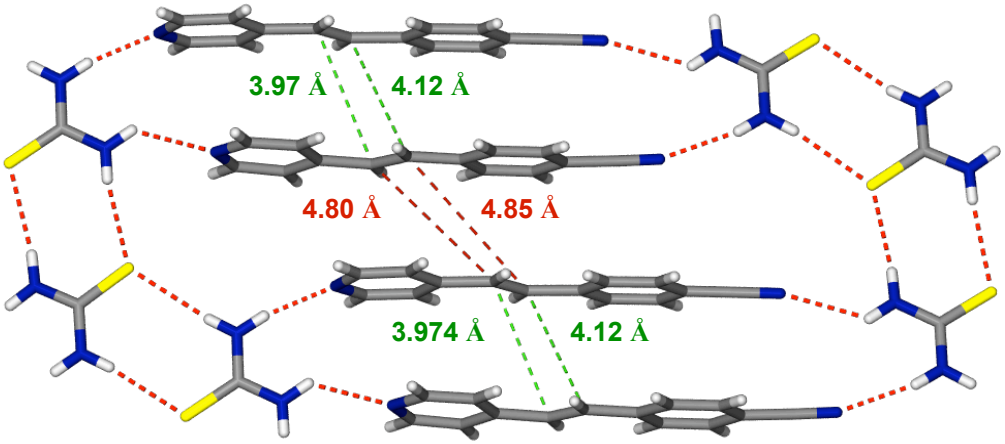


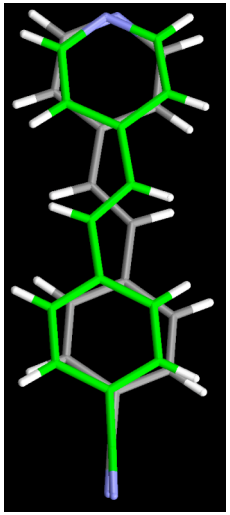


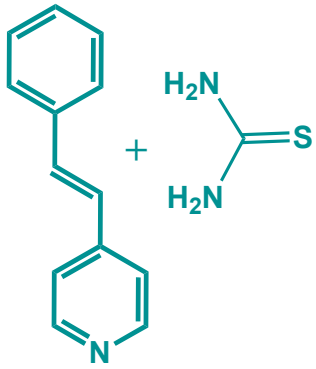
^{1}H NMR ($CDCl_3$) of cyclobutane protons in dimer products

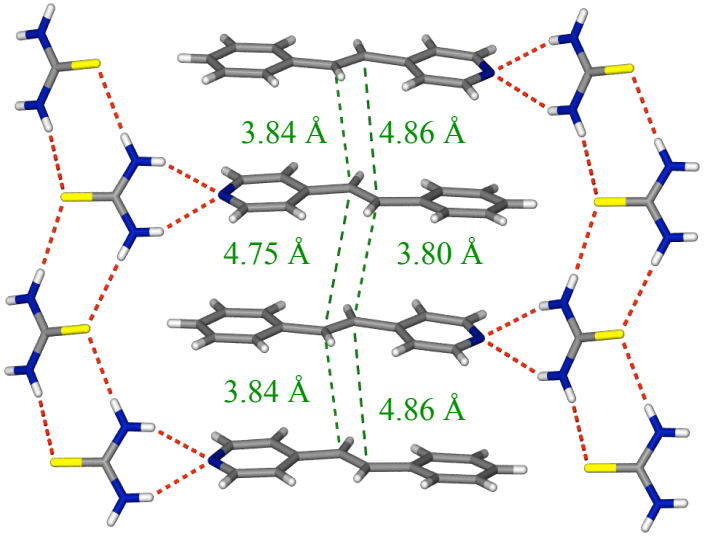
Anomalous orientation of 4-cyanostilbazole in thiourea co-crystals

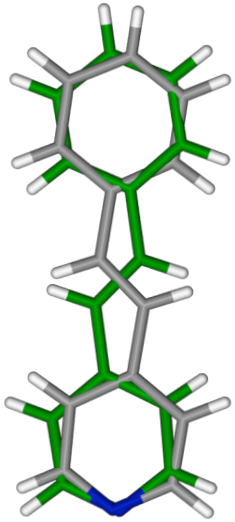


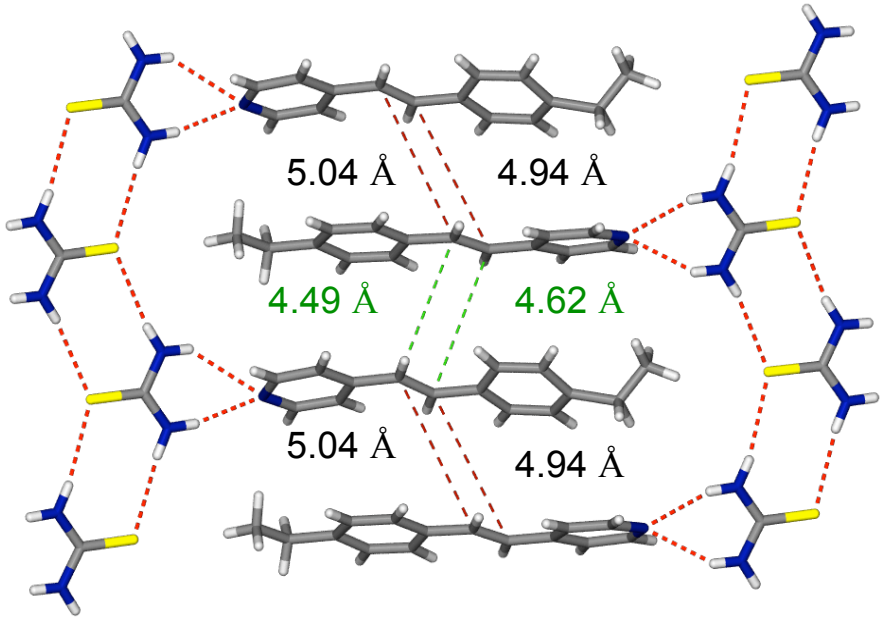


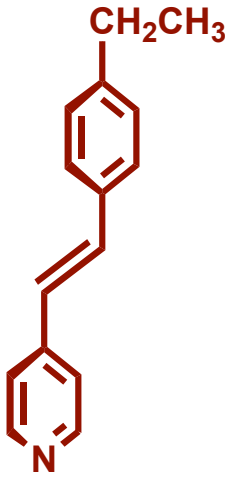




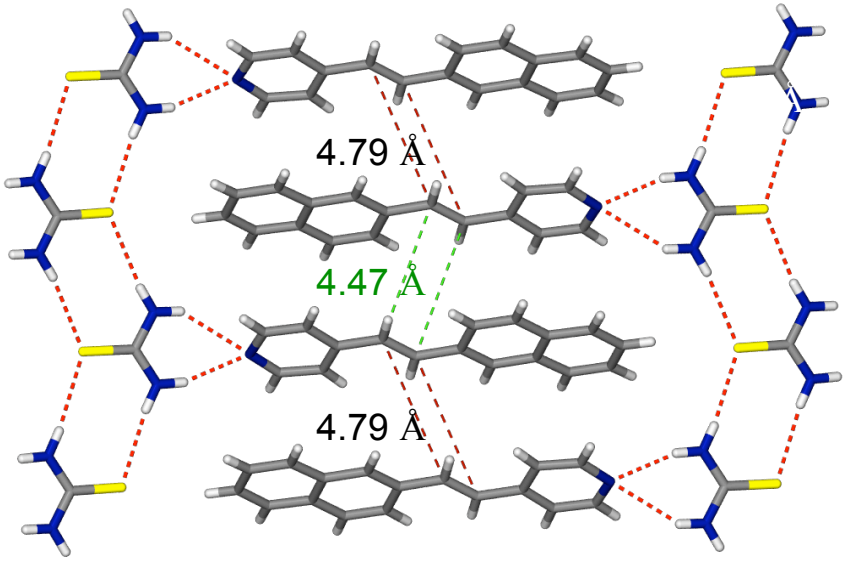


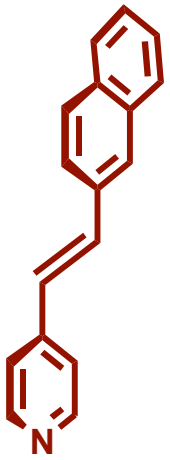






Does Not Dimerize





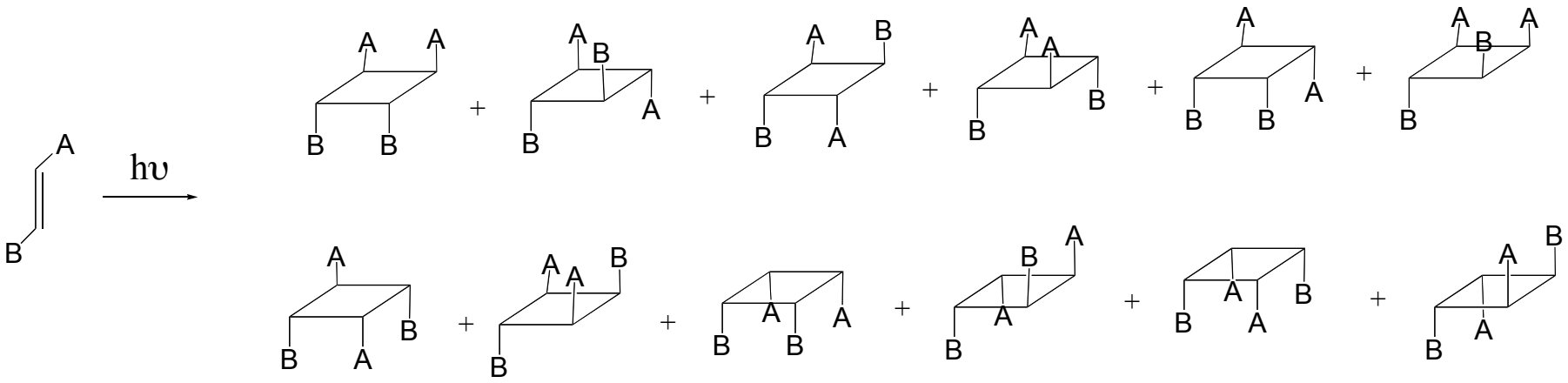
Does Not Dimerize

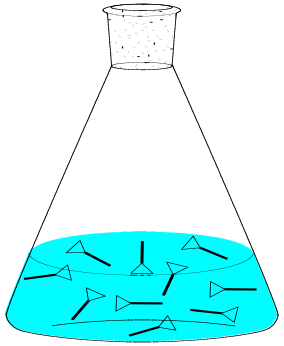
Acknowledgements

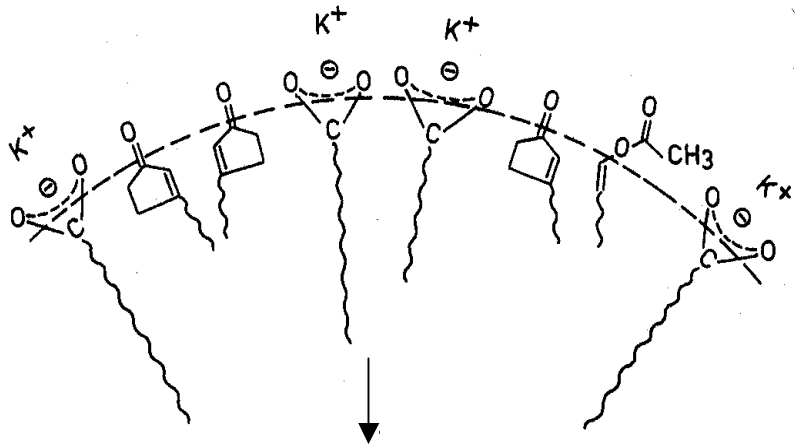


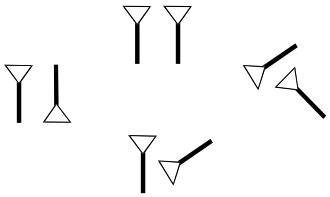
National Science Foundation
WHERE DISCOVERIES BEGIN

Controlling Products in Photocycloaddition Reactions

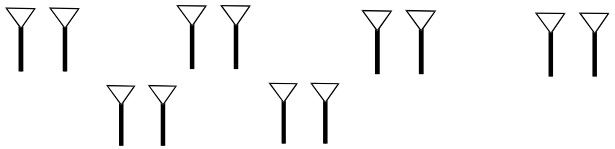








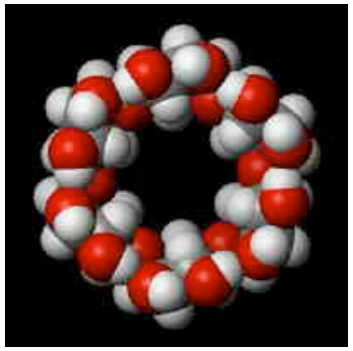
Poor alignment
Multiple products



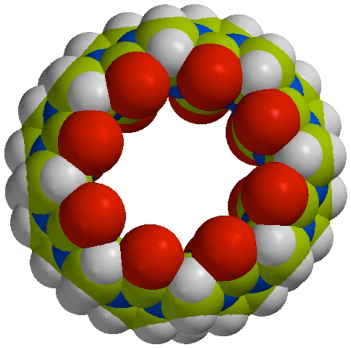
Highly aligned
Single product

de Mayo et al.,
JCS. Chem. Comm., 1980, 994

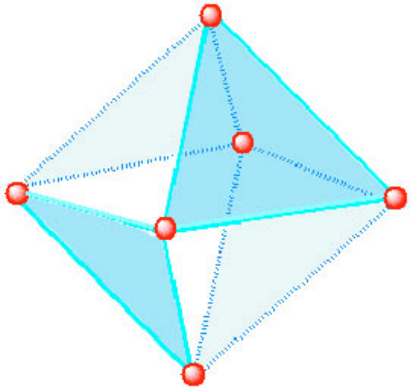
Water Soluble Hosts as Confined Media



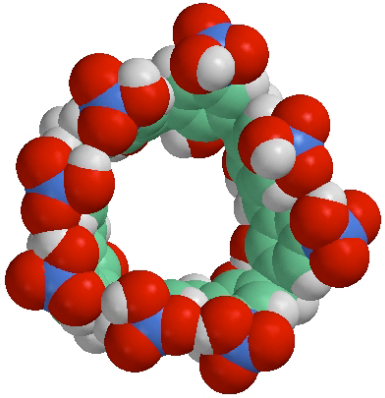
Cyclodextrins
Tabushi



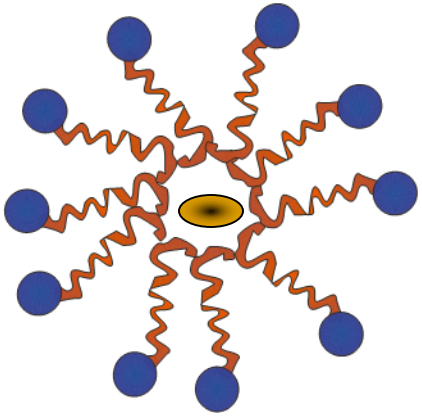
Cucurbiturils
Kim



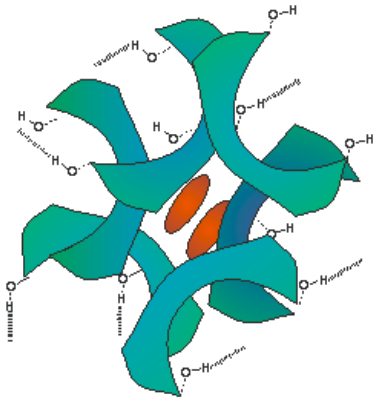
Pd Nano Cage
Fujita



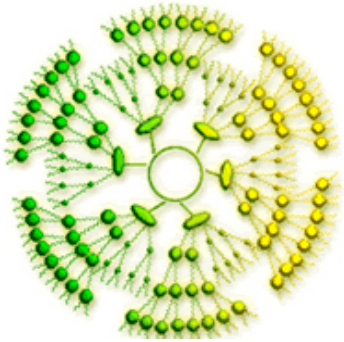
Calixarenes
Shinkai



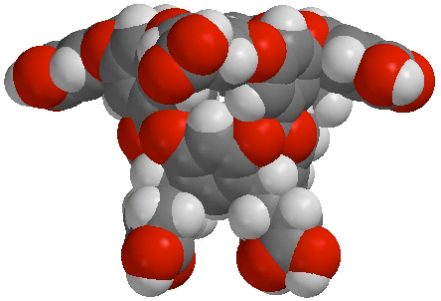
SDS / CTAC



NaCh / NaDCh

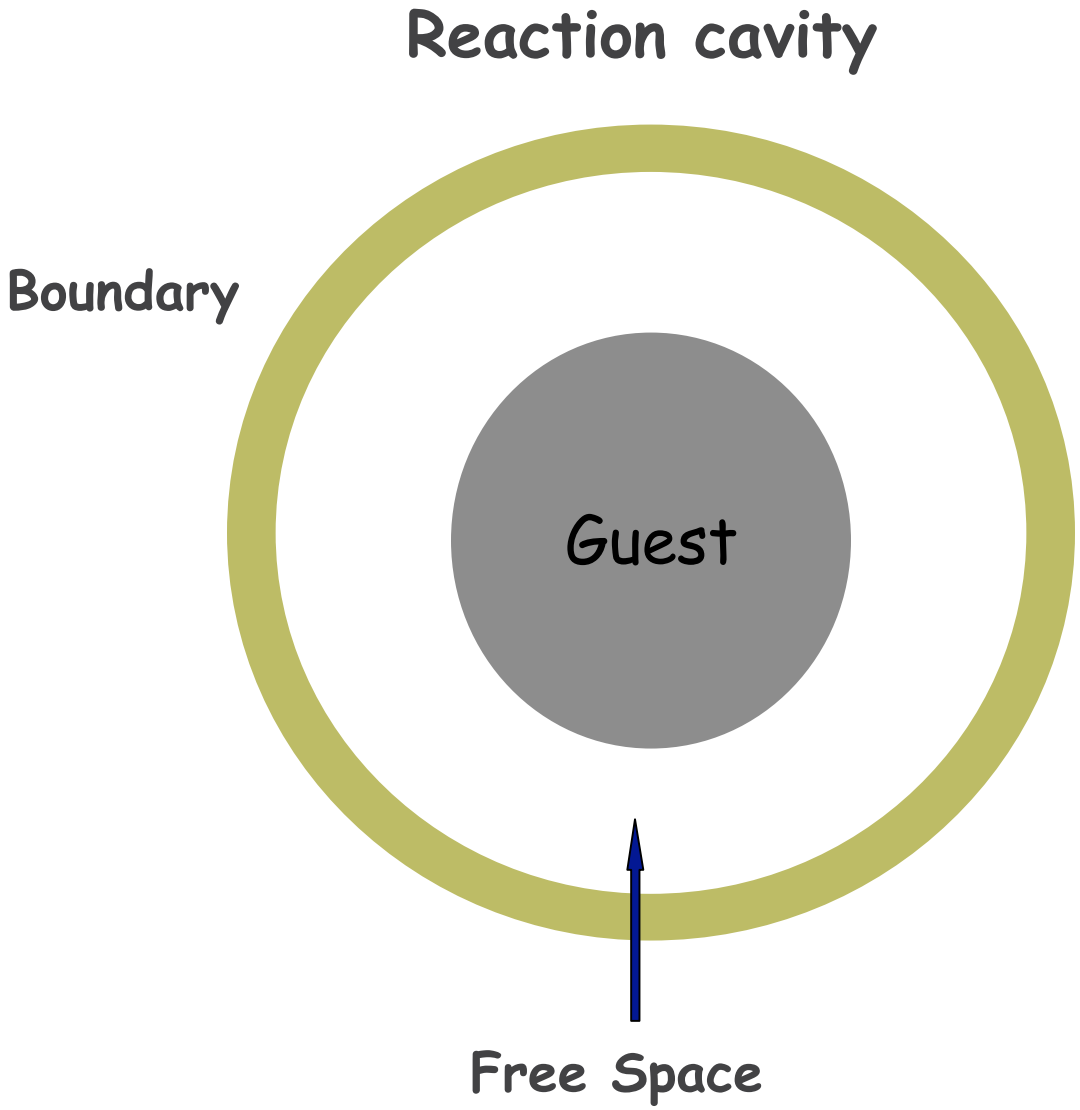


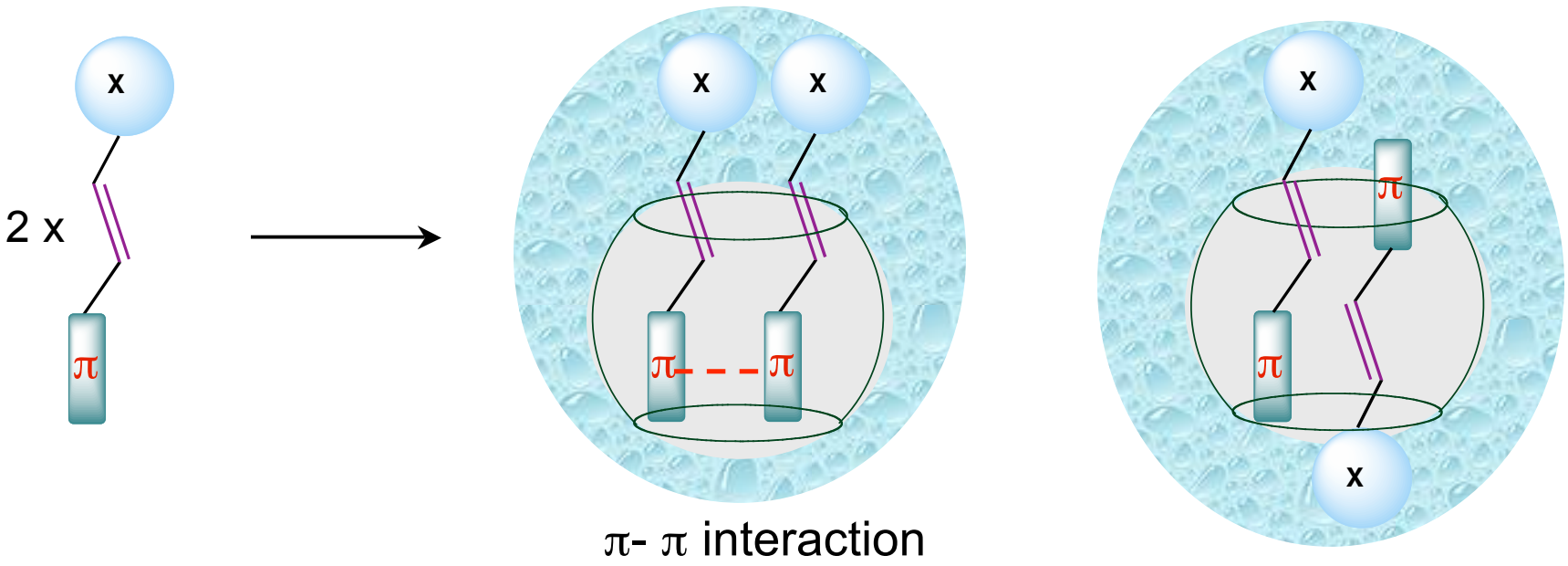
Dendrimers



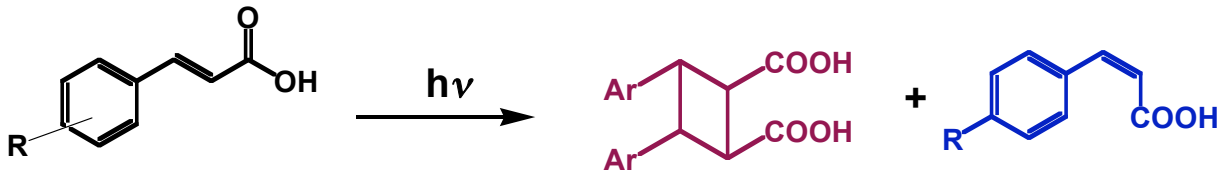
Octa acid

Supramolecular Containers



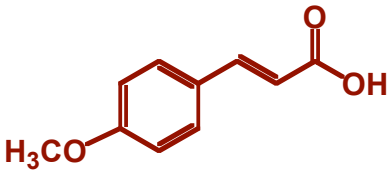

Syn head-head
Anti head-tail
2 x
x
π
x
x
π
π
x
π
π
x
π- π interaction

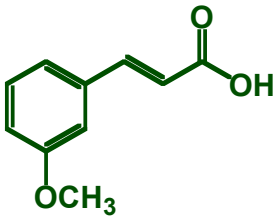
trans-Cinnamic acids photo inactive in solid state (γ-form)

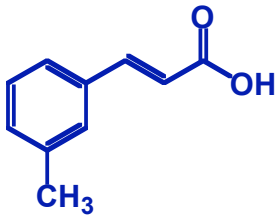


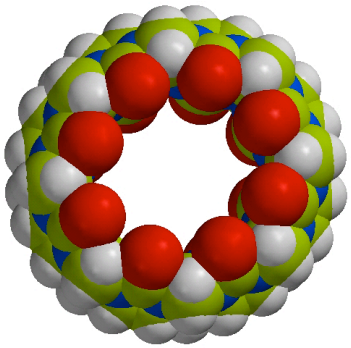
Ar = R-Ph

syn H-H dimer



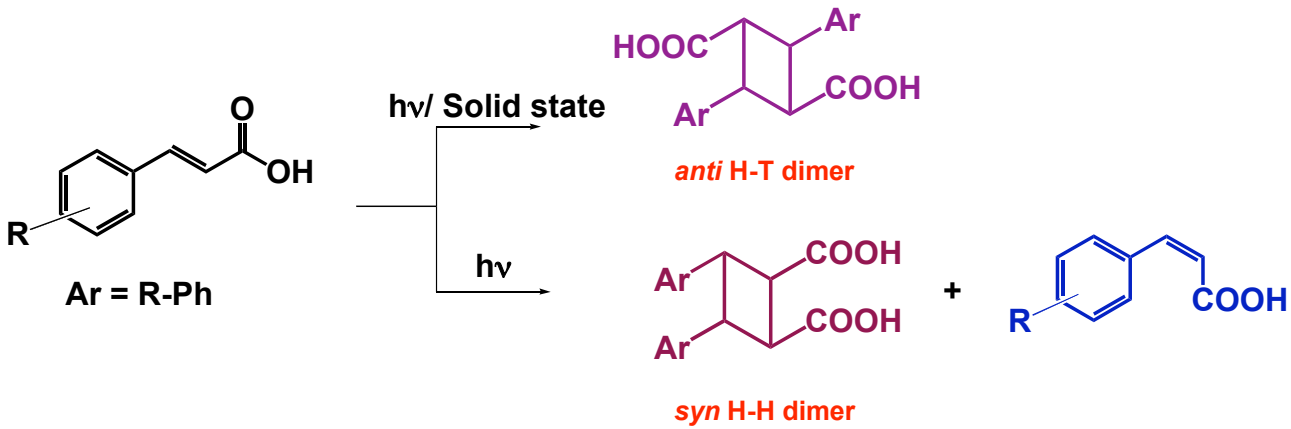


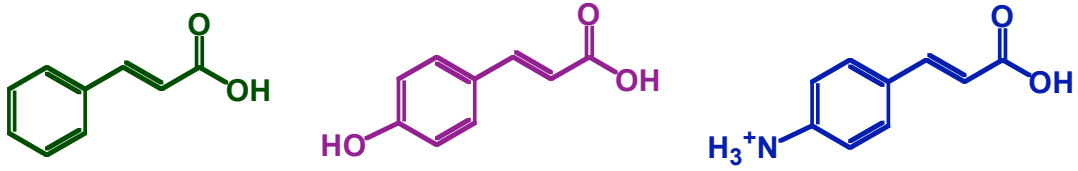


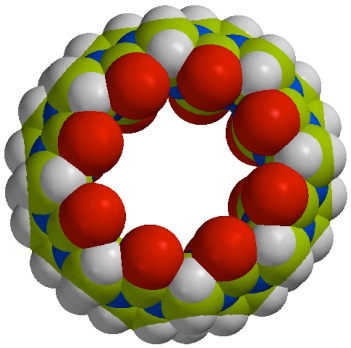


Ar	Solid state	% of dimer in CB[8]	% of cis isomer
R=4-OCH_3	--	72	28
R=3-OCH_3	--	72	28
R=3-CH_3	--	83	17

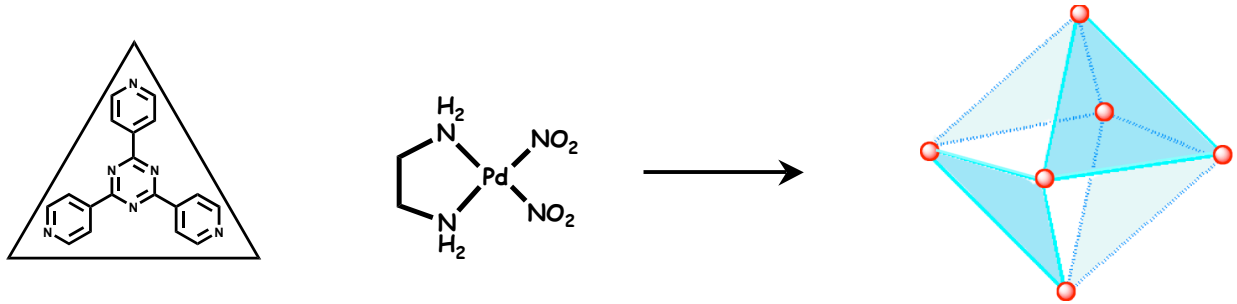
trans-Cinnamic acids that yield *anti* H-T dimer upon irradiation in solid state (α-form)

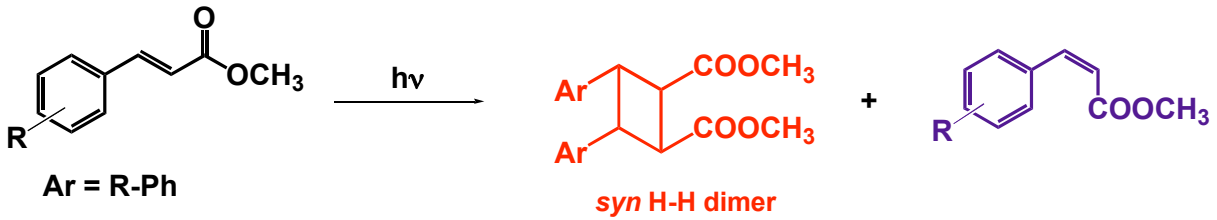






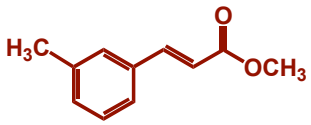
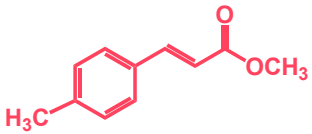
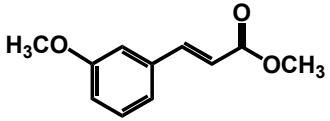
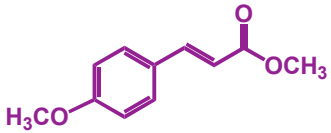
Ar	Solid state % of anti H-T dimer	% of Syn H-H dimer in CB[8]	% of cis isomer
R=H	100	54	46
R=4-OH	100	38	62
R=4-NH_3^+	100	88	12

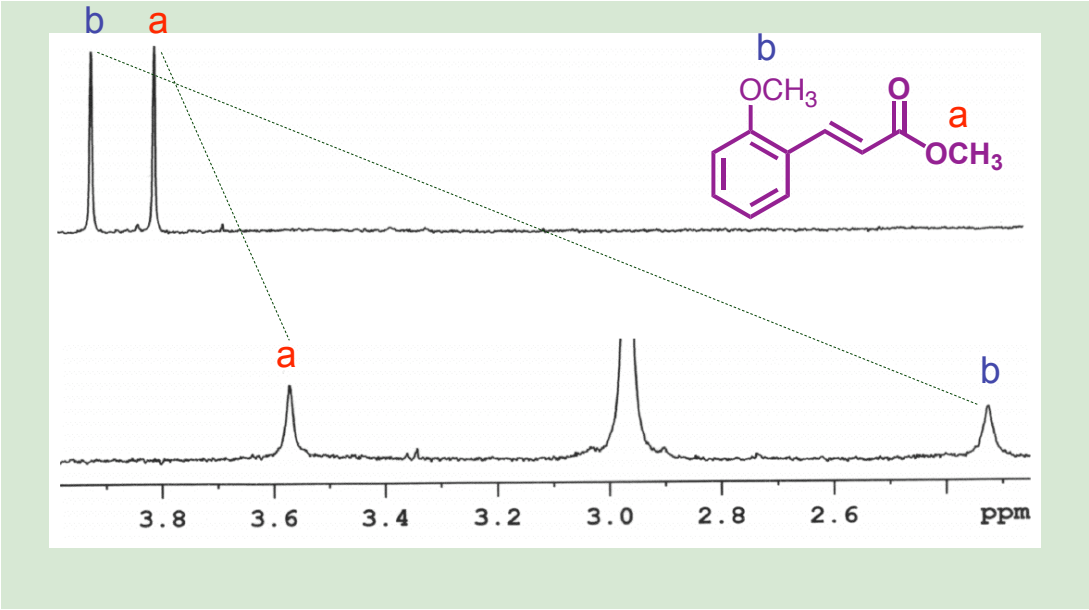


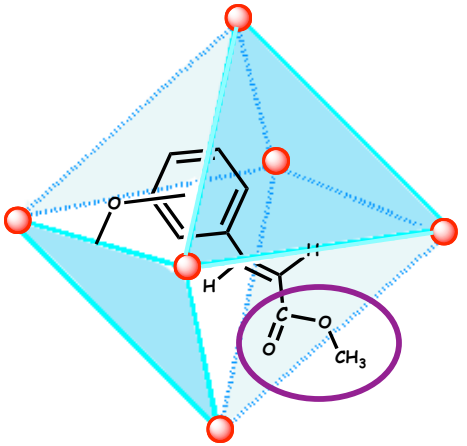


Ar = R-Ph

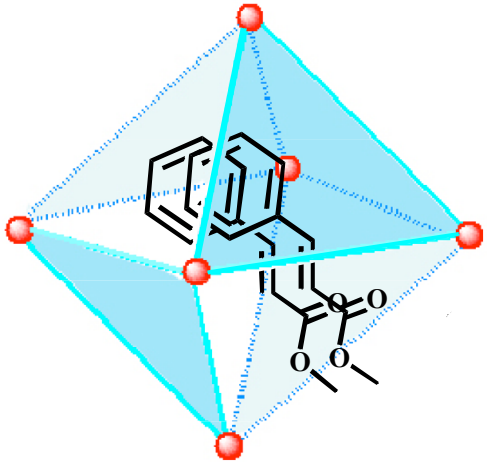
syn H-H dimer

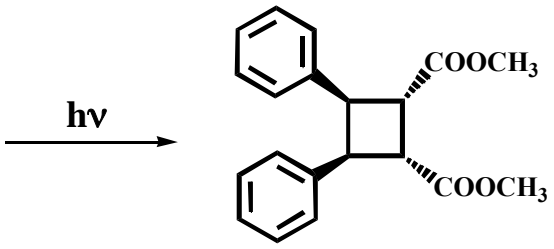
Substrate	% of Syn H-H dimer in nanocage	% of cis isomer
	63	37
	45	55
	42	58
	40	60



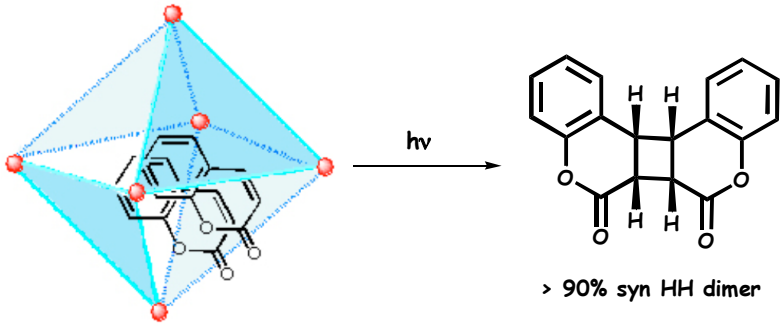


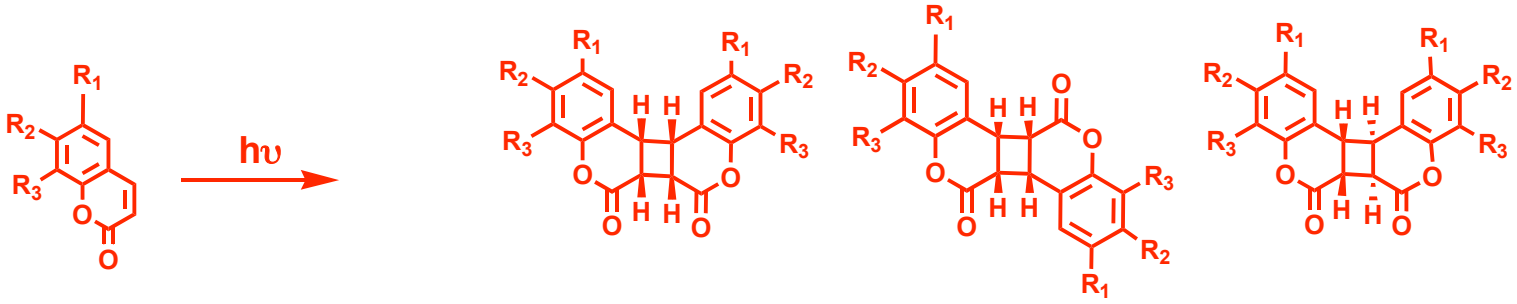
1) Top-^{1}H NMR of *O*-methoxy cinnamate in D_2O
2) Bottom- ^{1}H NMR of encapsulated *O*-methoxy cinnamate in Pd-Nanocage (0.5 eq.)



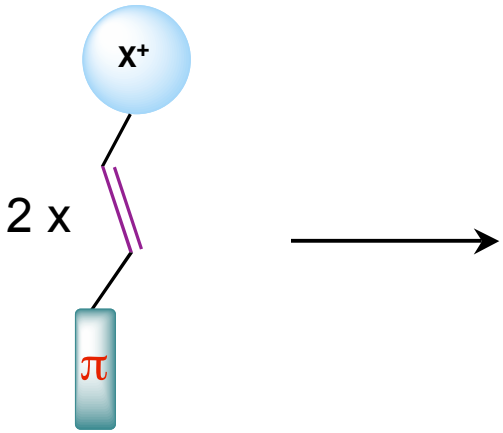


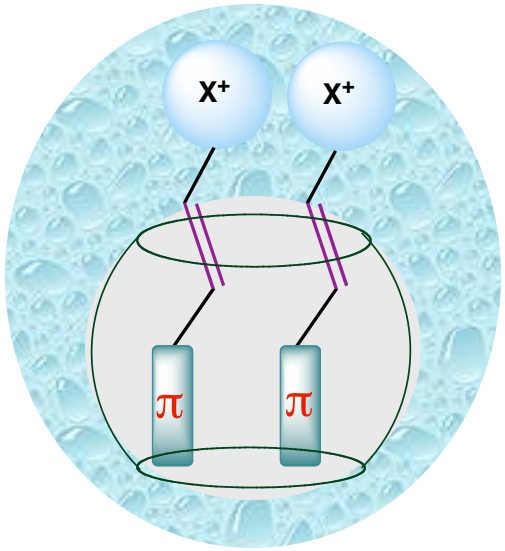
Syn head-head dimer



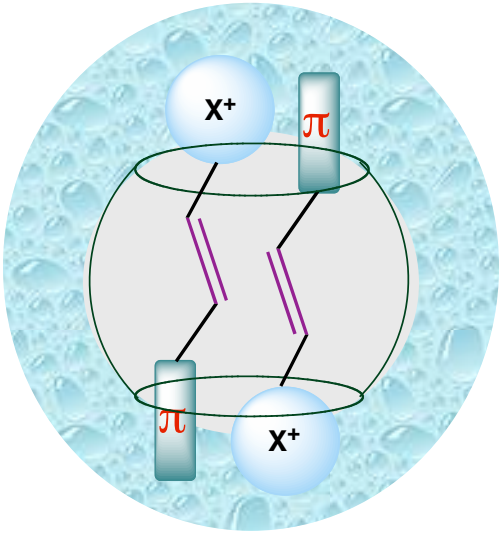


$R_1= R_2= R_3=H$	Water	60	40	-
	Pd-nanocage	>90	-	-
R_1=Me, $R_2=R_3=H$	Water	15	-	85
	Pd-nanocage	>90	-	-
R_2= OMe, $R_1= R_3=H$	Water		>90	-
	Pd-nanocage	>90	-	-
R_3=OMe $R_1=R_2=$ H	Water	Not soluble		
	Pd-nanocage	>90	-	-

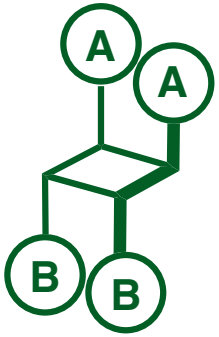




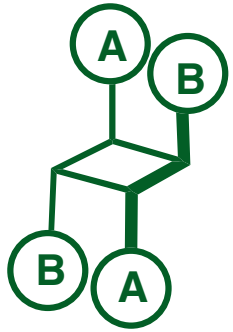
Charge repulsion



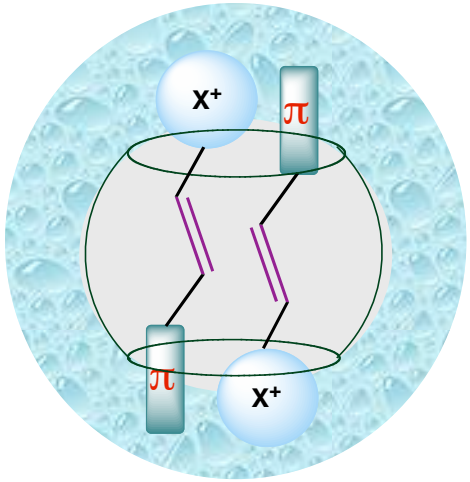
Cation-π interaction



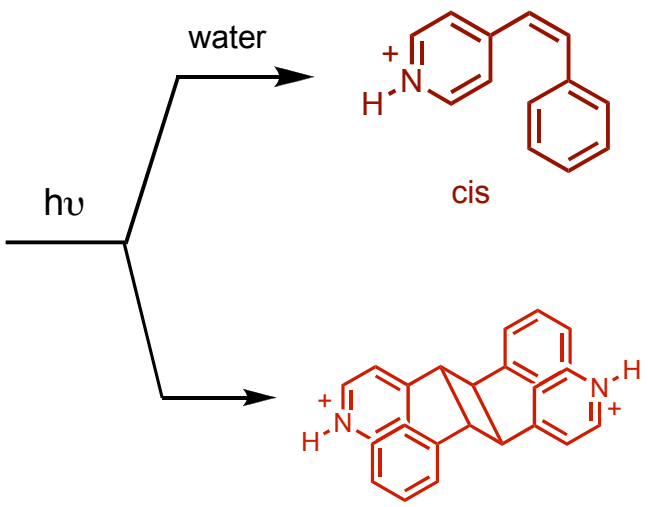
Syn H-H



Anti H-T



Cation-π interaction
Minimized ionic repulsion



cis

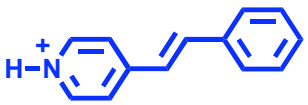
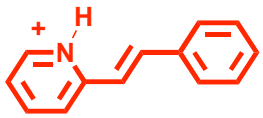
cyclized

anti H-T

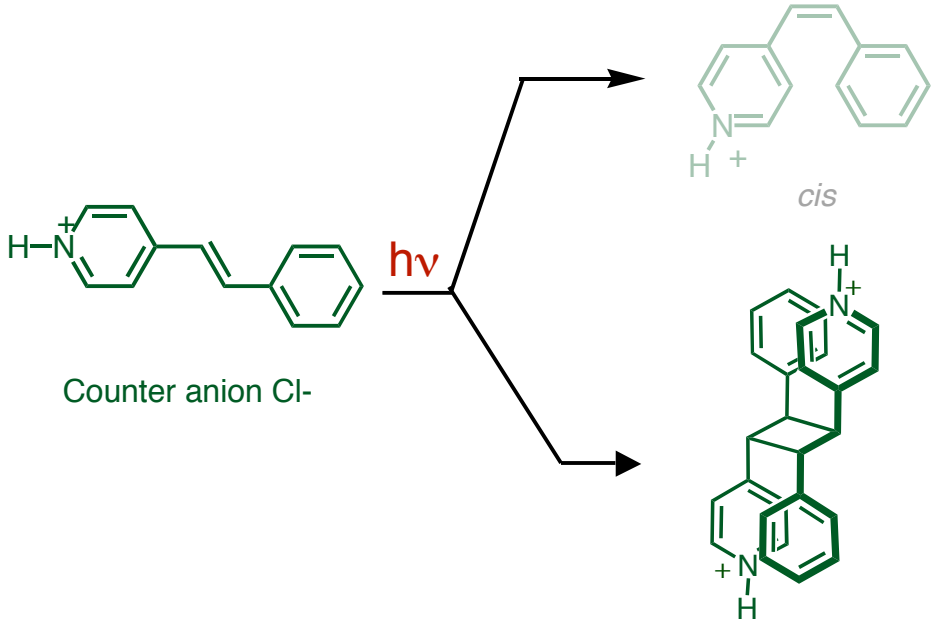
syn H-H

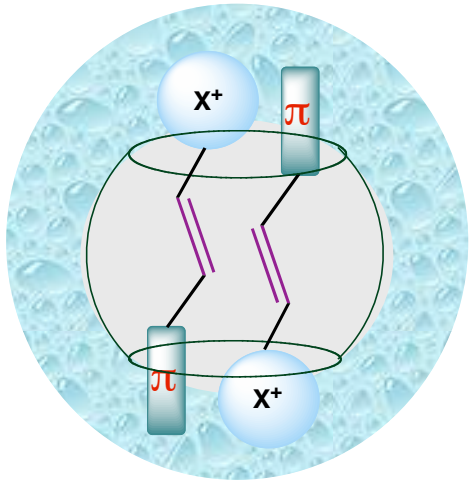
anti H-H

syn H-T

Guest	Medium	*anti* H-T	*syn* H-T	*cis*
	Water	03	02	95
	CB[8]	90	05	05
	Water	02	02	96
	CB[8]	82	00	18

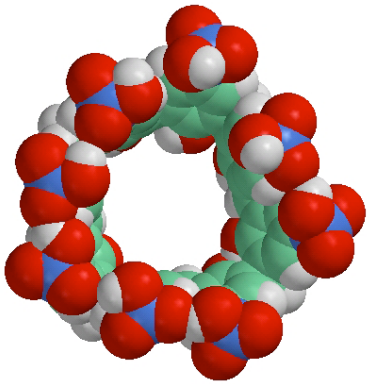
Photochemistry of Stilbazoles



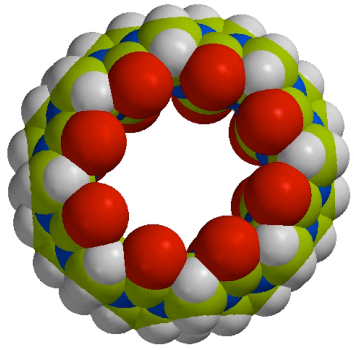


Cation- π interaction

Medium	*anti* H-T	*syn* H-T	*cis*
dil. HCl	13	16	71
PHBSA	24	14	62
$CA[6]SO_3H$	76	5	19
$CA[8]SO_3H$	86	2	12
CB[8]	90	--	10



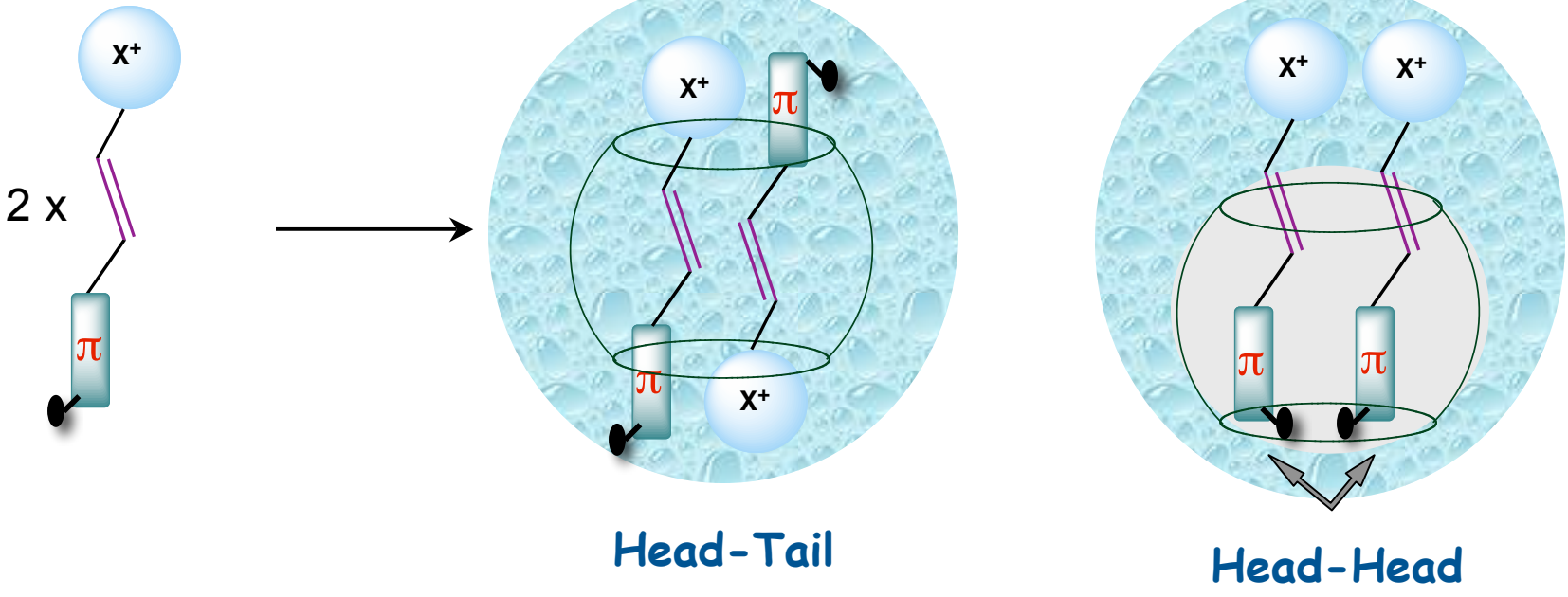
CA[8]



CB[8]

Cation- π interaction

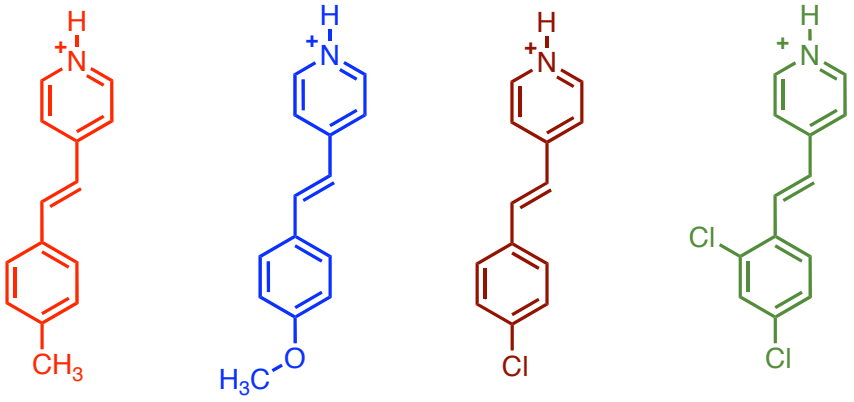
Charge repulsion



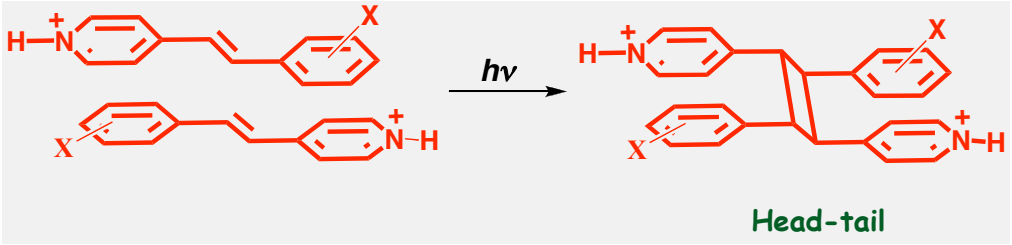
Head-Tail

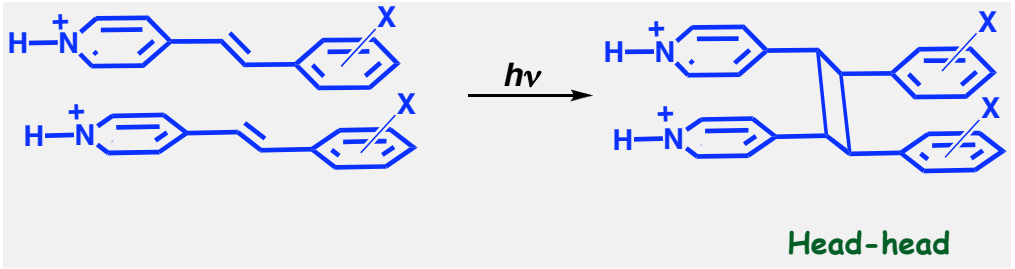
Head-Head

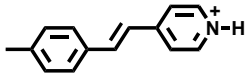
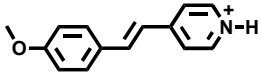
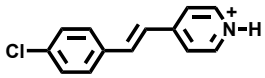
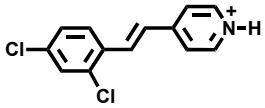
Can additional weak interactions (eg. Cl---Cl) alter the olefin pre-orientation?

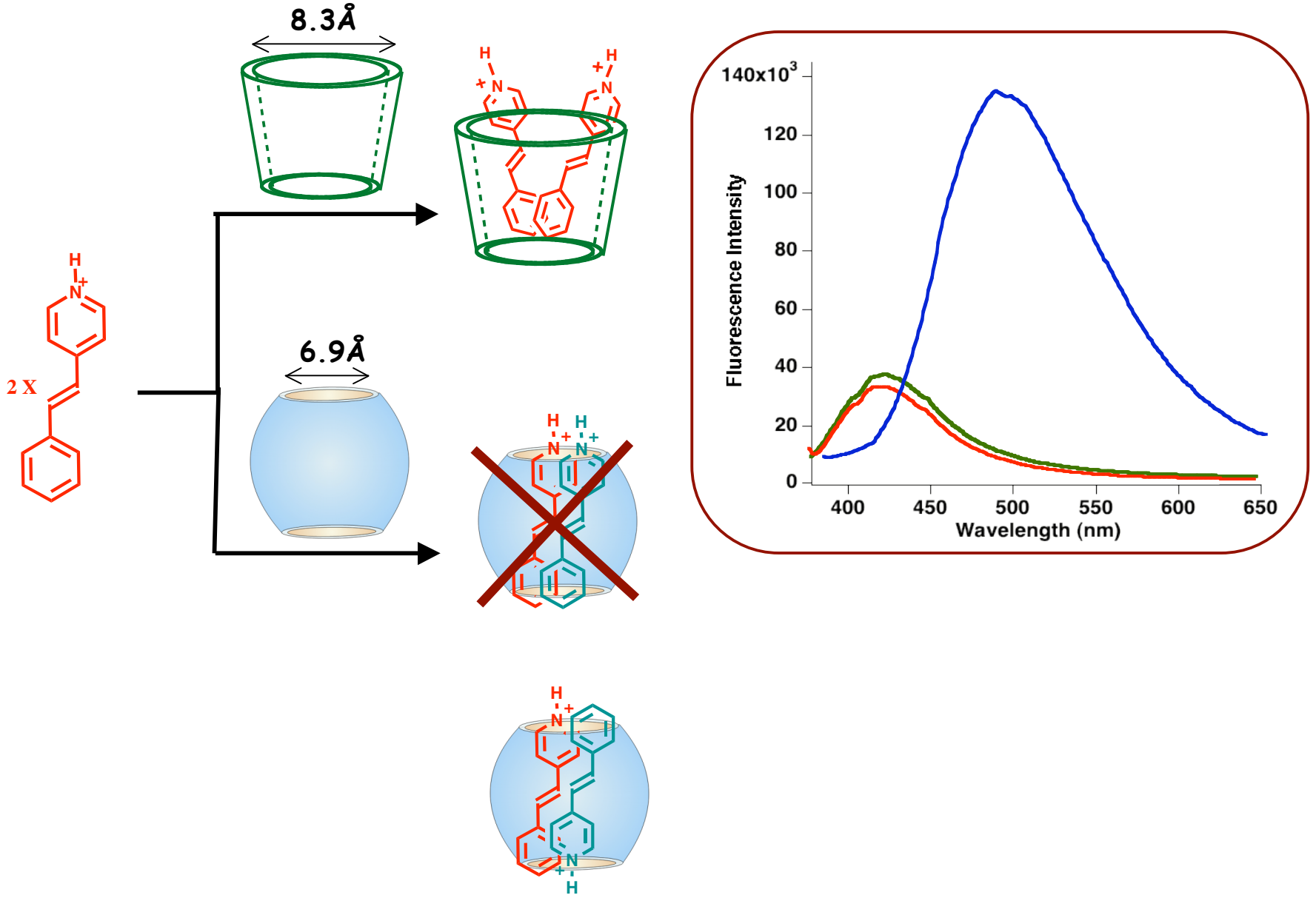


Counter anion Cl^-





Guest	Medium	Cis+ Cyclized	Head-tail	Head-head
	CB[8]	02	93	05
	γ-CD	48	27	19
	CB[8]	12	88	00
	γ-CD	26	74	--
	CB[8]	02	92	06
	γ-CD	27	5	68
	CB[8]	03	84	13
	γ-CD	25	8	67


8.3Å
6.9Å
2 X
140x10^3
120
100
80
60
40
20
0
Fluorescence Intensity
400
450
500
550
600
650
Wavelength (nm)

Acknowledgements

National Science Foundation
WHERE DISCOVERIES BEGIN