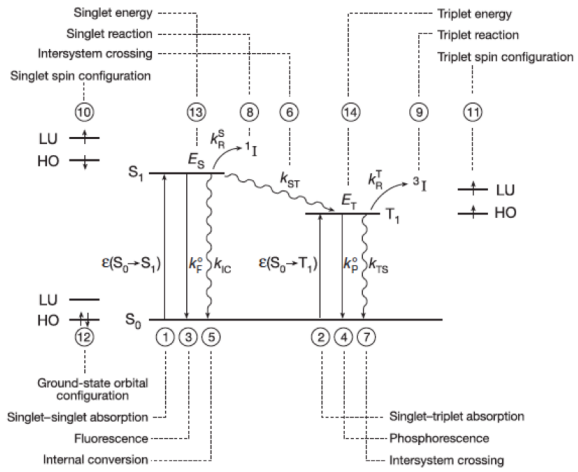
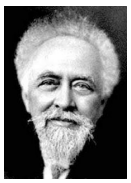
Supramolecular Photochemistry

Jablonski Diagram

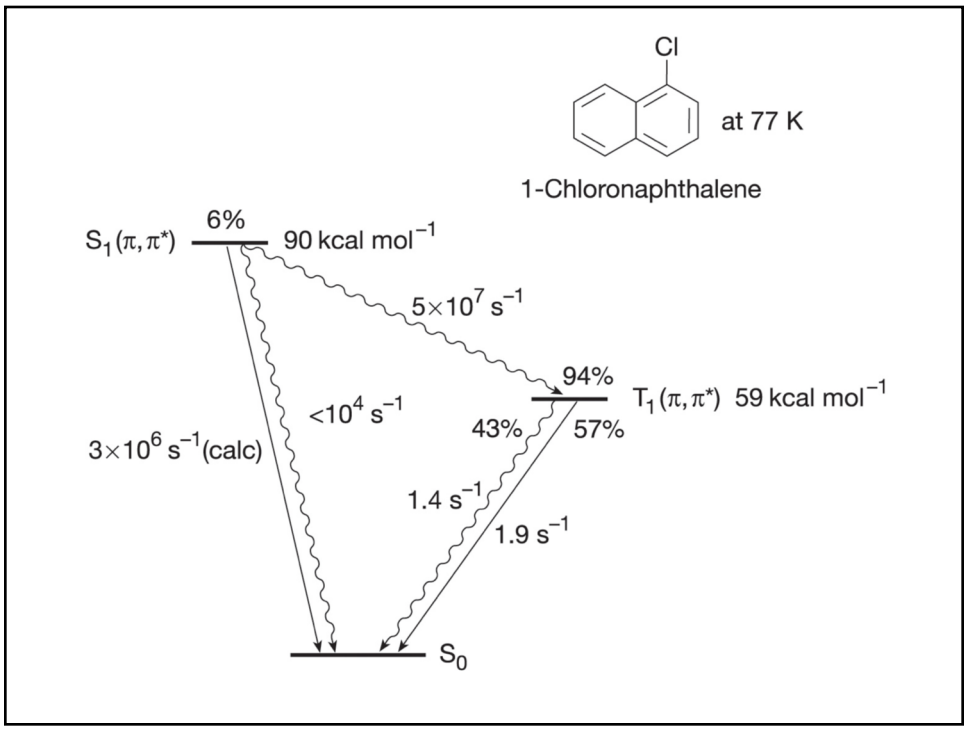


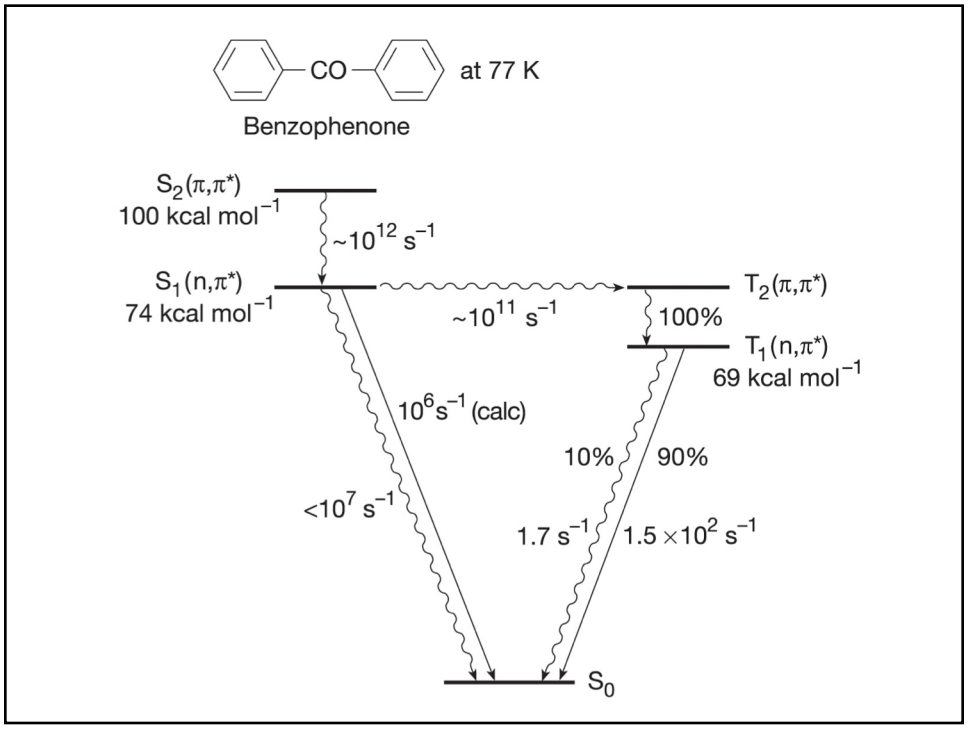
Alexander Jablonski (1898-1980)

F. Perrin



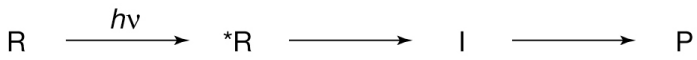
J. Perrin


Cl
at 77 K
1-Chloronaphthalene
6%
$S_1(\pi,\pi^*)$
90 kcal mol^{-1}
5×10^7 s^{-1}
94%
$T_1(\pi,\pi^*)$ 59 kcal mol^{-1}
$<10^4$ s^{-1}
3×10^6 s^{-1}(calc)
43%
57%
1.4 s^{-1}
1.9 s^{-1}
S_0

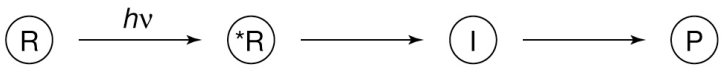

CO
at 77 K
Benzophenone
$S_2(\pi,\pi^*)$
100 kcal mol^{-1}
~10^{12} s^{-1}
$S_1(n,\pi^*)$
74 kcal mol^{-1}
~10^{11} s^{-1}
$T_2(\pi,\pi^*)$
100%
$T_1(n,\pi^*)$
69 kcal mol^{-1}
10^6s^{-1} (calc)
10%
90%
$<10^7$ s^{-1}
1.7 s^{-1}
1.5×10^2 s^{-1}
S_0

Molecular and Supramolecular Photochemistry

Molecular photochemistry



Supramolecular photochemistry



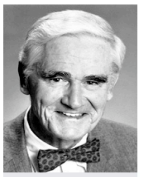
R represents a guest molecule. The circle represents a host molecule.

The beginnings of supramolecular organic chemistry: Cram, Lehn, Pedersen

Chemistry

The Nobel Prize in Chemistry 1987

"for their development and use of molecules with structure-specific interactions of high selectivity"



Donald J. Cram

1/3 of the prize

USA

University of California
Los Angeles, CA, USA

b. 1919
d. 2001

Jean-Marie Lehn

1/3 of the prize

France

Université Louis Pasteur
Strasbourg, France;
Collège de France
Paris, France

b. 1939

Charles J. Pedersen

1/3 of the prize

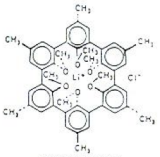
USA

Du Pont
Wilmington, DE, USA

b. 1904
(in Fusan, Korea)
d. 1989

Crown ether complex
according to Pedersen

cryptand complex
= cryptate
according to Lehn



host-guest complex
according to Cram

The Nobel Prize in Chemistry 2016

“for the design and synthesis of molecular machines"

Jean-Pierre Sauvage

J. Fraser Stoddart

Bernard L. Feringa

7

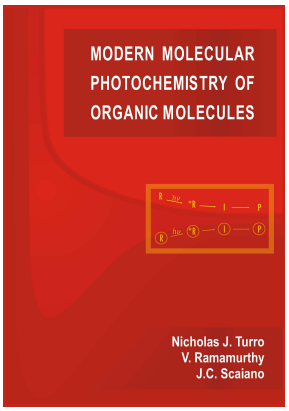
Supramolecular Photochemistry

R. Breslow

J. M. Lehn

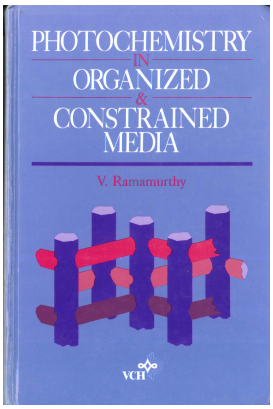
N. J. Turro

Reference books

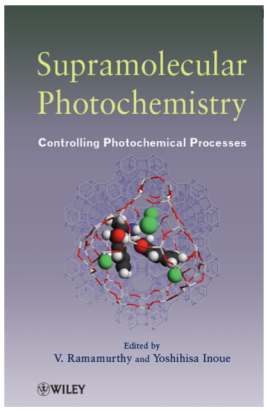


2010

Chapter 13



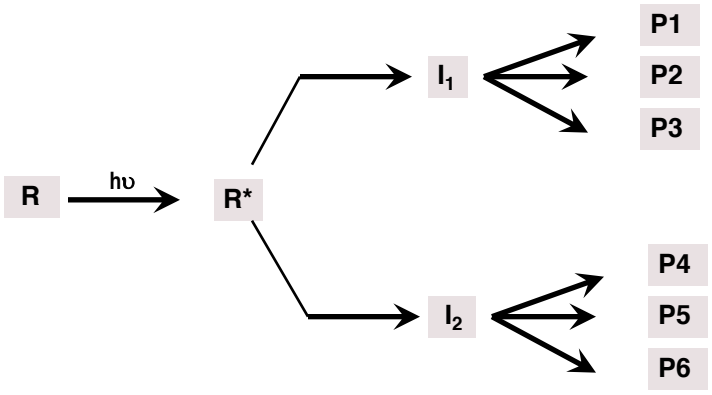
1991



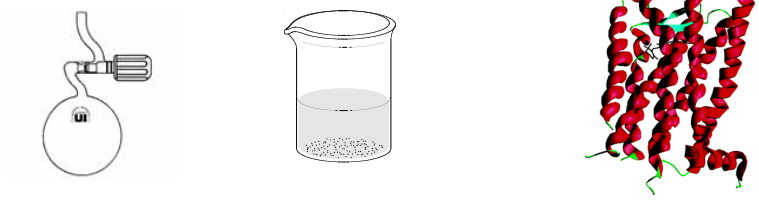
2011

Supramolecular Hosts

Photochemistry often yields multiple products



Medium Matters



Gas phase

Solution
(solvent + solute)

Rhodopsin

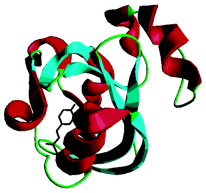
Increasing selectivity

How do biological media enforce selectivity?

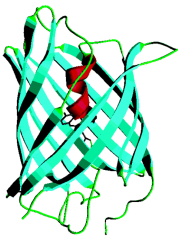
Highly selective geometric isomerization occurs within a protein medium

Rhodopsin

Bacteriorhodopsin



Photoactive yellow protein

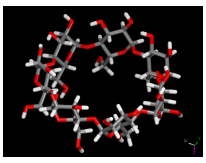


Green fluorescent protein

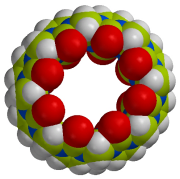
How do a biological media enforce selectivity?

- by restricting the rotational and translational motions
- by pre-organizing the reactants
- by controlling the extent and the location of free space within a reaction cavity

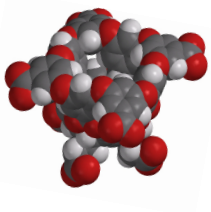
Chemistry in bowls, baskets, cages and cavities



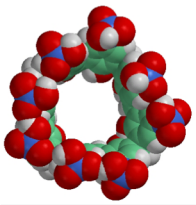
Cyclodextrins



Cucurbiturils

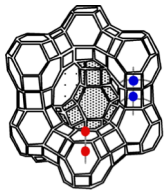


Octa acid(OA)

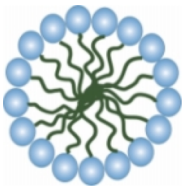


Calixarenes

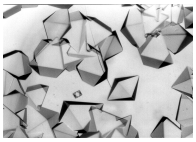
Dendrimers



Zeolites

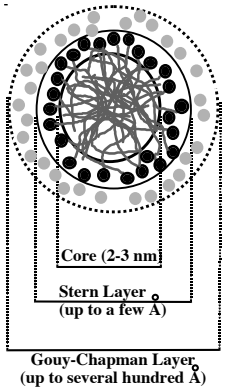


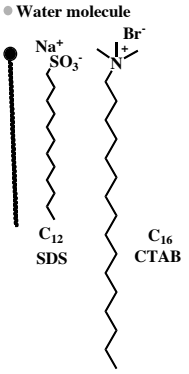
Micelles

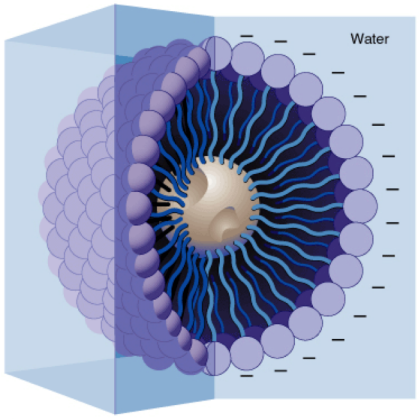


Crystals

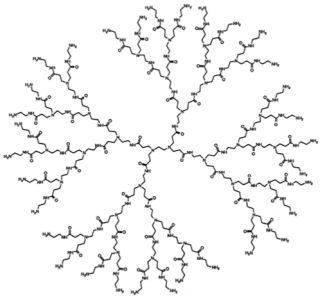
Micelles





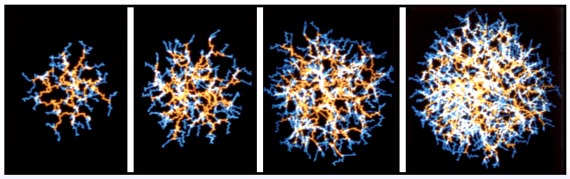


Dendrimers: covalent micelles



A dendrimer: a hyperbranched polymer

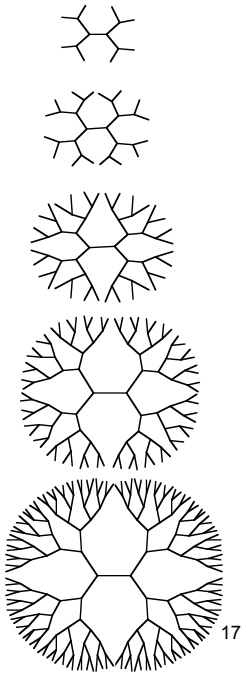
Generation increasing ➔



16

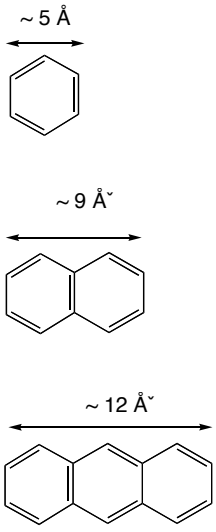
Generations of dendrimers

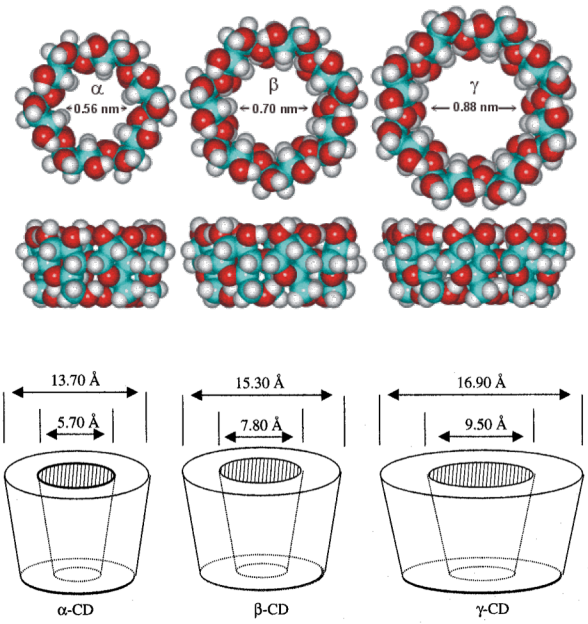
generation	surface groups	diameter (Å)	separation of the surface groups (Å)	surface groups
0.5	6	27.9	12.4	8
1.5	12	36.2	12.8	16
2.5	24	48.3	12.7	32
3.5	48	66.1	12.6	64
4.5	96	87.9	11.5	128
5.5	192	103.9	10.3	256
6.5	384	126.8	9.8	512
7.5	768	147.3	7.7	1024



17

Water soluble organic hosts: Cyclodextrins





Water soluble organic hosts: Cucurbiturils

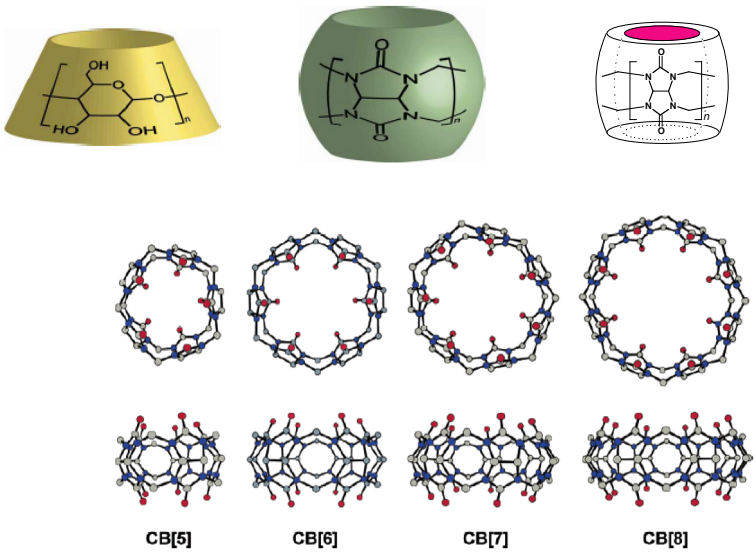
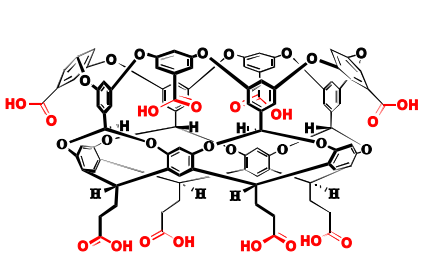
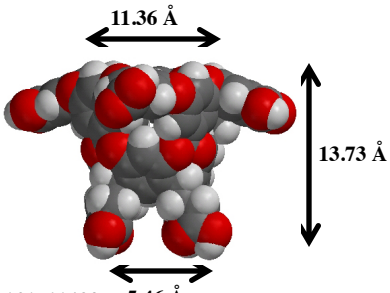
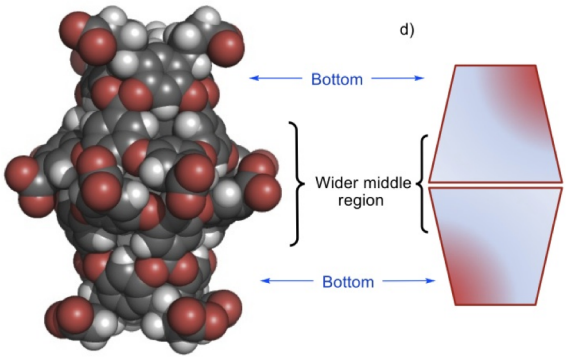


FIGURE 1. X-ray crystal structures of CB[*n*] (*n* = 5–8). Color codes: carbon, gray; nitrogen, blue; oxygen, red.

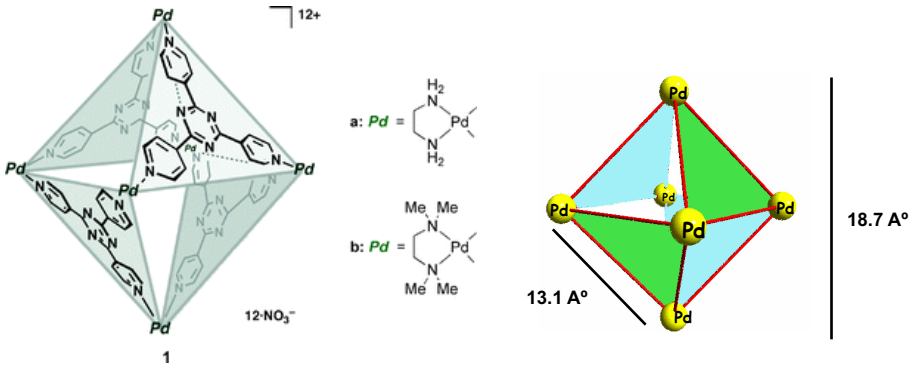




C. L. D. Gibb, and B. C. Gibb, *J. Am. Chem. Soc.*, 2004, *126*, 11408.

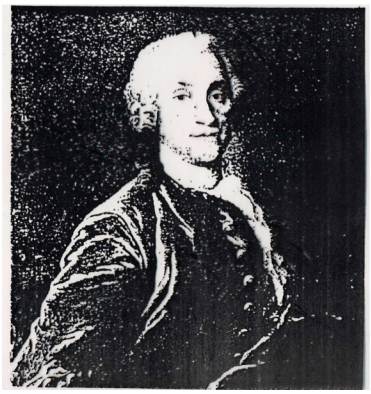


Water soluble inorganic host: Fujita's Pd host



21

Discovery of zeolites



Baron Cronstedt 1722-1765

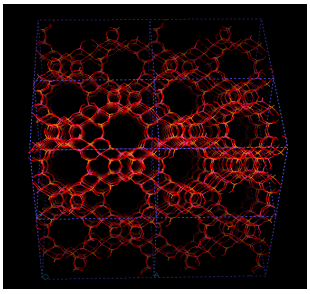
A zeolite, as found in Nature

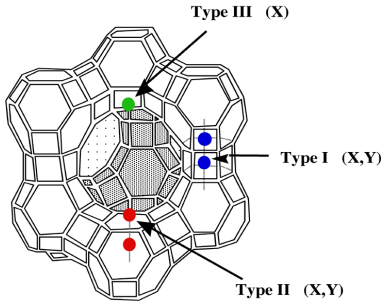
Cronstedt discovered "boiling stones" which he called "zeolites" from the Greek: zeo (boil) and lithos (stone).

22

Characteristics of Faujasites (Zeolites)

$M_x(AlO_2)_x\ (SiO_2)_y.ZH_2O$



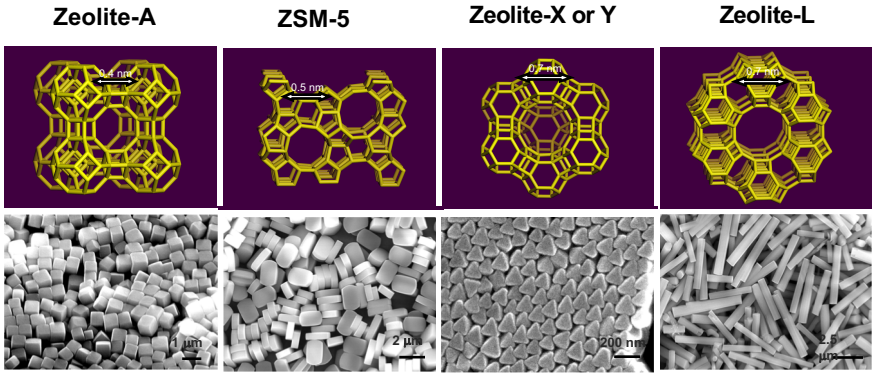


- Microporous solid
- Large surface area
- Well defined channels/cages
- Si/Al ratio = 2.4
- Type I - 4 cations /supercage
- Type II- 4 cations /supercage

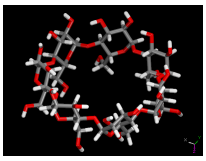
23

Zeolites: Sythetic

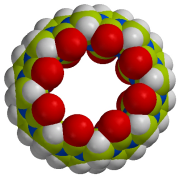
More than 65% of the earth's crust consists of 3D crystalline polyaluminosilicates (3D-CPAS): feldspar, zeolite, and ultramarine. Zeolite is a class of 3D-CPAS having nanochannels and nanocavities.



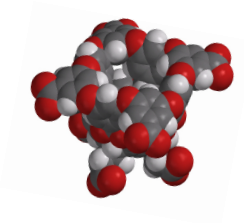
Chemistry in bowls, baskets, cages and cavities



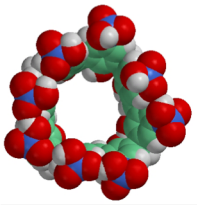
Cyclodextrins



Cucurbiturils

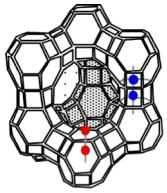


Octa acid(OA)

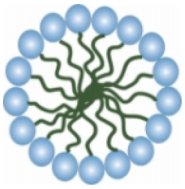


Calixarenes

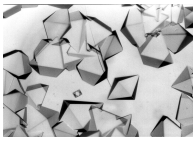
Dendrimers



Zeolites

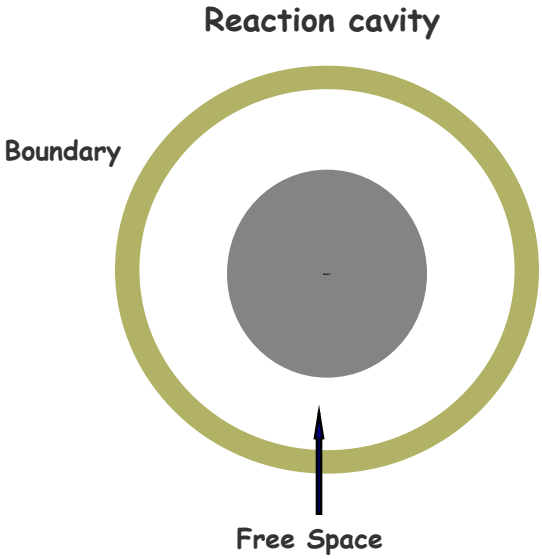


Micelles



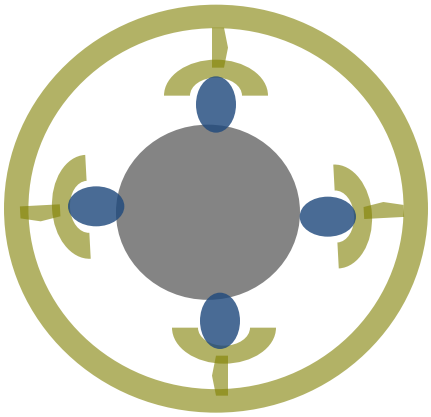
Crystals

Supramolecular Containers



26

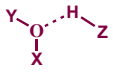
Role of Weak Interactions



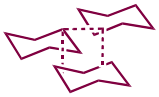
Cation---π

π---π

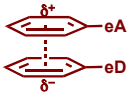
C-H---π



Hydrogen bond



van der Waals



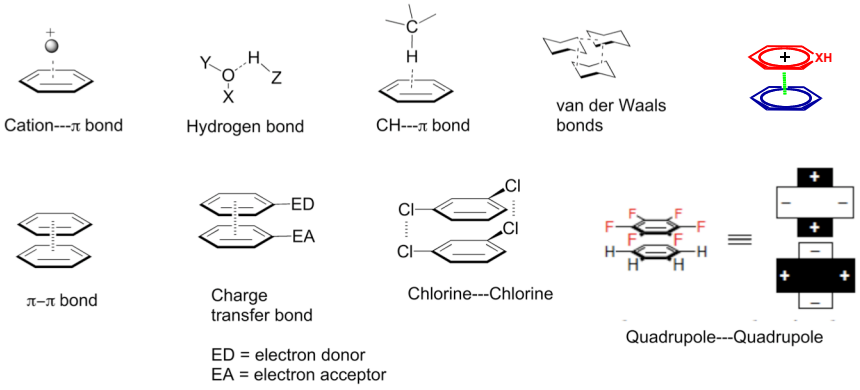
Charge transfer

27

Supramolecular Weak Interactions

Relevant Weak Interactions in Supramolecular Chemistry

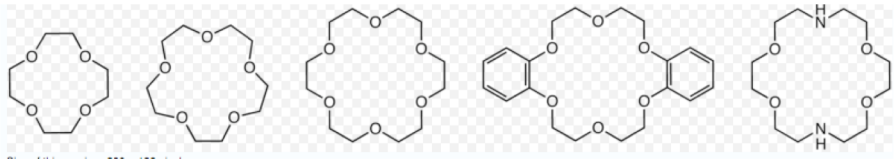
Examples of weak intermolecular interactions (typical energies vary from <1 kcal mol^{-1} to ~10 kcal mol^{-1})

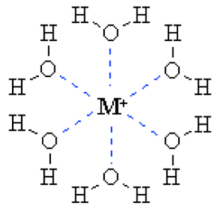


Ion-Dipole

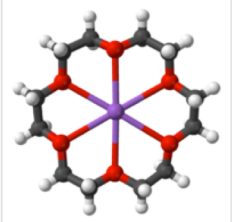
Quite useful for molecular recognition and sensing

~ 10 - 50 kcal/mol (50-200 kJ/mol)





hydration of a metal ion



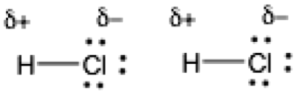
18-crown-6 K^+

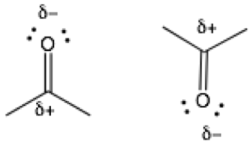
Water like interior
Alkane exterior

Dipole-Dipole

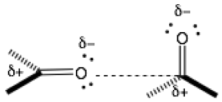
Interaction between molecules with permanent dipoles

~ 1-15 kcal/mol (5-50 kJ/mol)





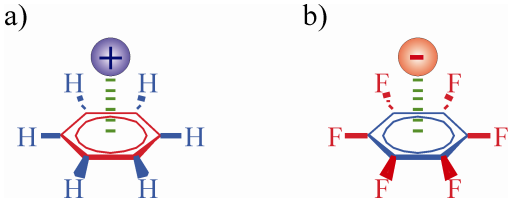
or



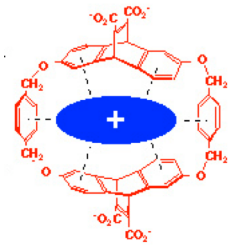
Ketones are a good example but their low bp shows this is a relatively weak interaction

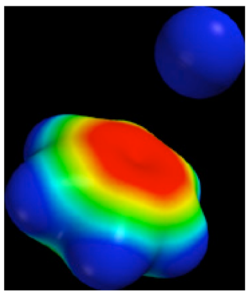
Bp ~56° C

Cation-π and Anion -π



~ 1 - 20 kcal/mol

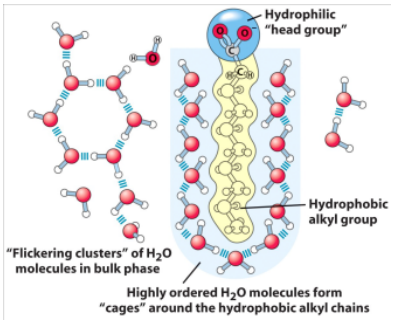




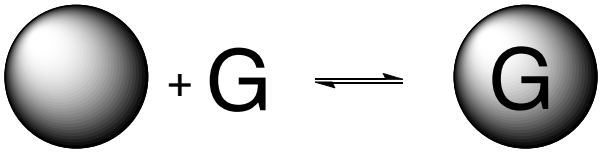
~ 25% of Tryptophan residues in proteins make cation-pi interactions

Hydrophobic Effects

The hydrophobic interaction is mostly an entropic effect originating from the disruption of highly dynamic hydrogen bonds between molecules of liquid water by the nonpolar solute.



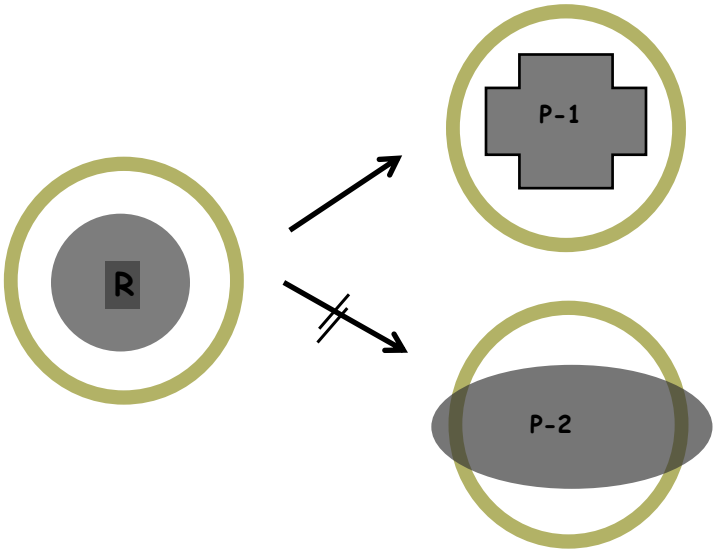
The guest@host paradigm

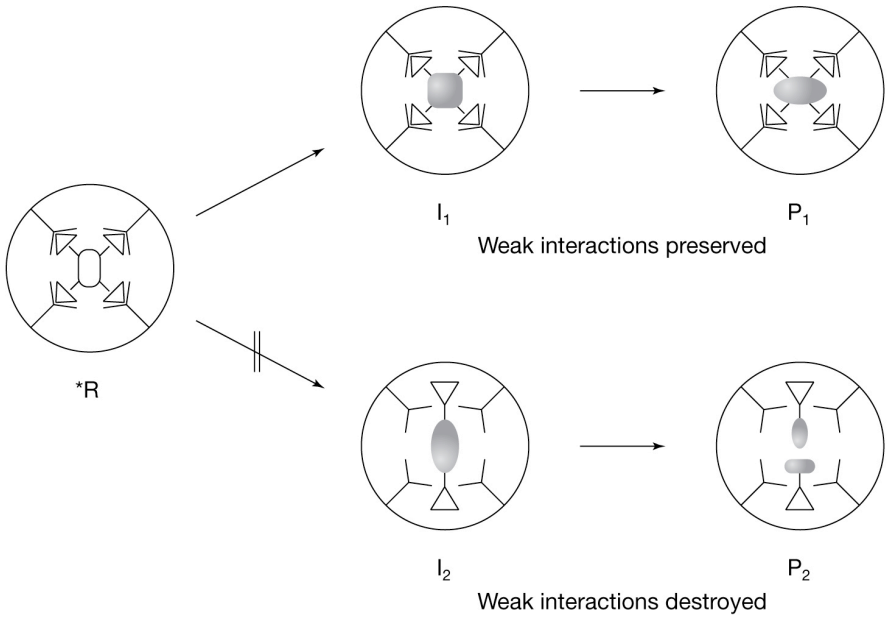


We'll be using this paradigm to discuss supramolecular systems

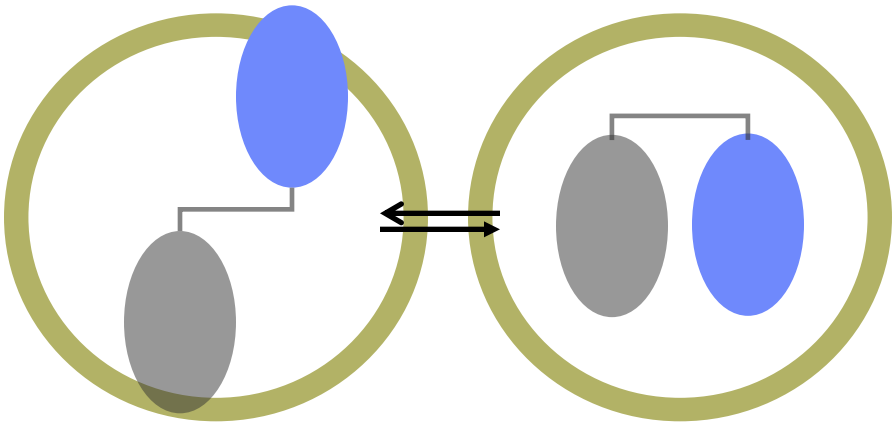
34

Role of Free Space: Product Must Fit the Reaction Cavity

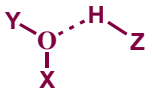




Conformational Control and Rotational Restriction



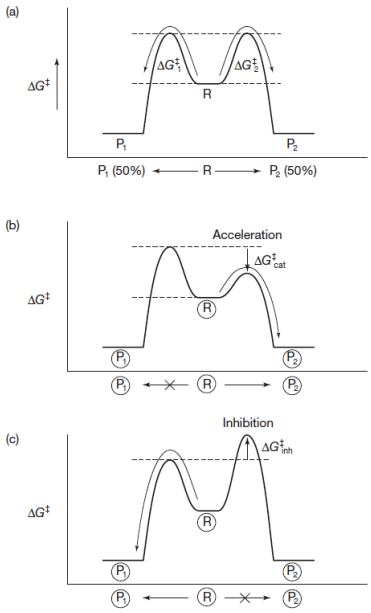
Pre-organization Through Weak Interactions



Hydrogen bond

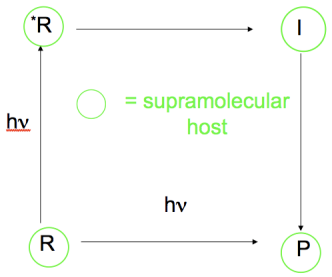
38

Energy diagram representation of supramolecular control of a reaction



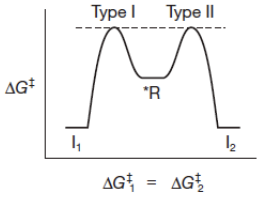
The top reaction (a) is indiscriminate since the activation energies for R going to P_1 or P_2 are identical

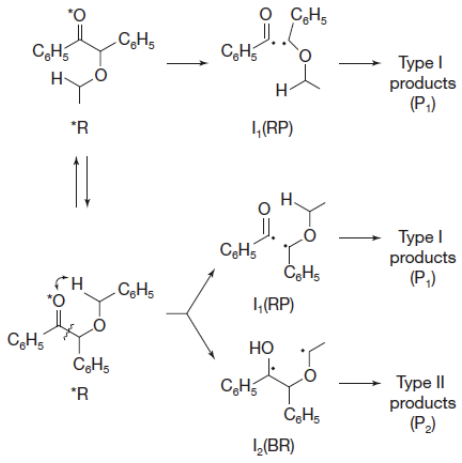
The "circle" (host) can accelerate (b) or inhibit (c) the rate of a reaction



39

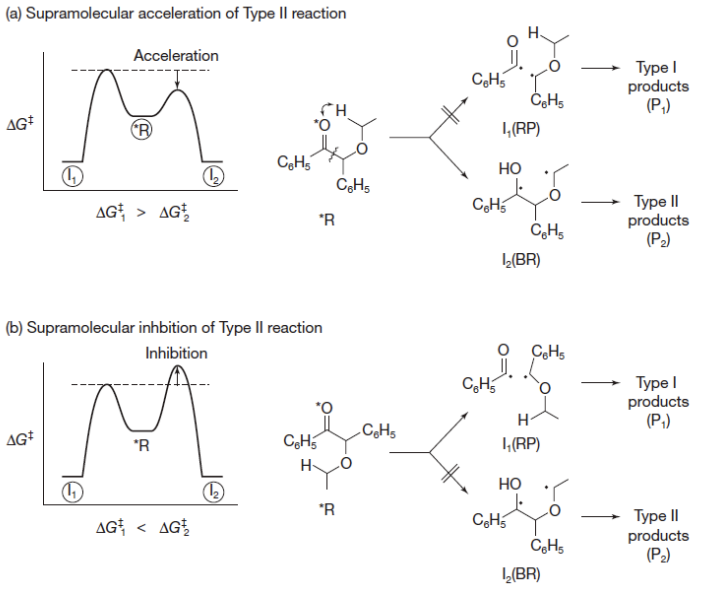
An exemplar of supramolecular control of a photoreaction with two competing paths





40

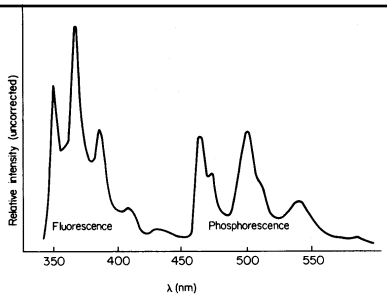
Acceleration and inhibition of the Type II photoreaction

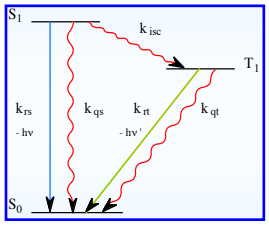


41

Supramolecular Photophysics

- Manipulating photophysics of organic molecules through weak interactions and confinement
- Use of organic photophysics in understanding supramolecular structures
- Supramolecular organic photohysics: Sensors, molecular motors, etc.



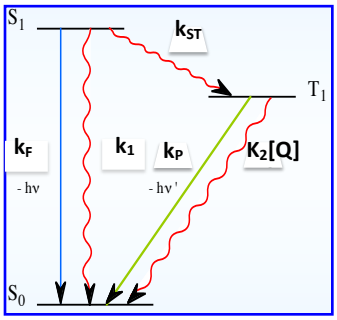


Fluorescence:

- High radiative rate constant, 10^{-10} to 10^{-8} s^{-1}
- Precursor state (S_1) has a short lifetime
- Not susceptible to quenching

Phosphorescence:

- Low radiative rate constant, 10^{-6} to 10 s^{-1}
- Precursor state (T_1) has long lifetime
- Very much susceptible to quenching
- Emission quantum yield depends on S_1 to T_1 crossing



$$^*R(S_1) \xrightarrow{k_{ST}} {}^*R(T_1) \xrightarrow{k_P} S_0 + h\nu_P$$

$$^*R(S_1) \xrightarrow{k_1} \text{not } ^*R(T_1)$$

$$^*R(T_1) \xrightarrow{k_2[Q]} \text{not } h\nu_P$$

The heavy atom effect on spin transitions

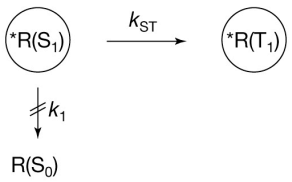
The "heavy atom" effect is an "atomic number" effect that is related to the coupling of the electron spin and electron orbit motions (spin-orbit coupling, SOC).

Most commonly, the HAE refers to the rate enhancement of a spin forbidden photophysical radiative or radiationless transition that is due to the presence of an atom of high atomic number, Z.

The heavy atom may be either internal to a molecule (molecular) or external (supramolecular).

Strategy to record phosphorescence at room temperature through supramolecular approach

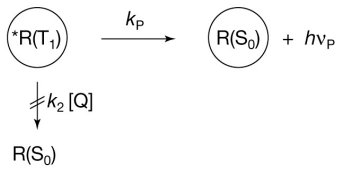
Stage 1



Heavy atom effect mainly on k_{ST} so that $k_{ST} > k_1$

Make more triplets through the heavy atom effect

Stage 2

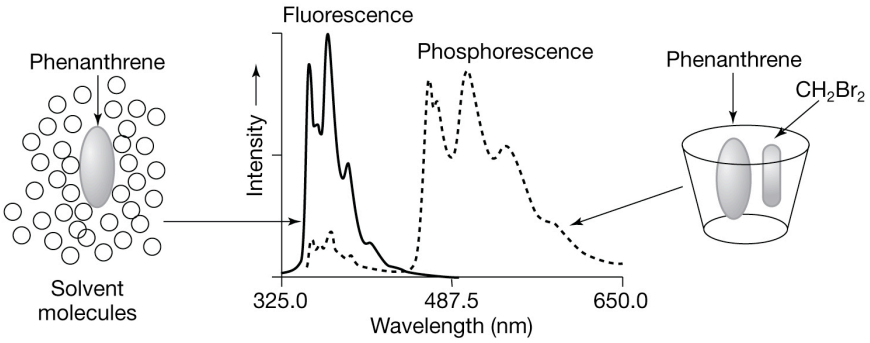


Heavy atom effect mainly on k_P so that $k_P > k_2$ [Q]

Make triplets emit faster in competition with quenching processes

Cyclodextrins as hosts

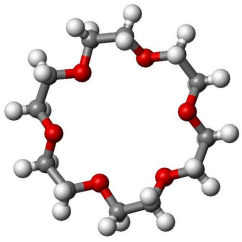
Phenanthrene@Cyclodextrin: effect of CH_2Br_2 as co-guest

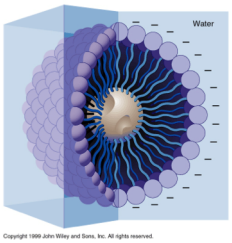


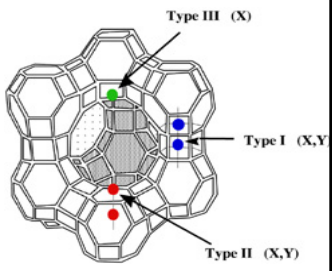
Induced Intersystem Crossing Depends on the SOC: Cations as the heavy atom pertuber

Atom	Ionic Radius of the Cation (Å)	Spin-Orbit Coupling ζ cm^{-1}
Li	0.86 (+)	0.23
Na	1.12	11.5
K	1.44	38
Rb	1.58	160
Cs	1.84	370
Tl	1.40	3410
Pb	1.33 (2+)	5089

Crown ethers, micelles and zeolites contain cations





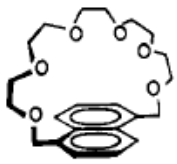


External heavy atom effect: Crown ether approach

Table II. Estimates[a,b] of Rate Constants for Excited-State Processes of 1,5-Naphtho-22-crown-6 (**1**) in Alcohol Glass[c] at 77 K with Alkali Metal Chloride Salts Added in 5:1 Molar Excess (Crown at 1.00×10^{-4} *F*)

Salt added	$10^{-6}k_f$	$10^{-6}k_{nr}$	$10^{2}k_p$[d]	k_{dt}[d]
None	3.1	25	8.7	0.37
NaCl	2.6	32	6.7	0.41
KCl	2.3	35	5.8	0.39
RbCl	1[e]	52	12.	0.50
CsCl	1[e]	670	81.	1.57

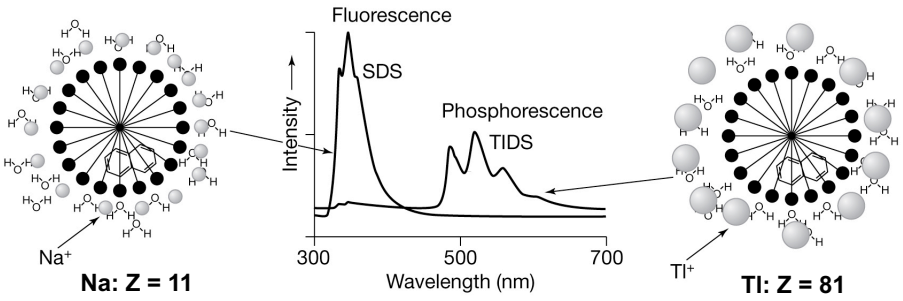
[a] All rate constants in s^{-1}. [b] $k_f = \phi_f\tau_f^{-1}$; $k_{nr} = (1 - \phi_f)\tau_f^{-1}$; $k_p = \phi_p(1 - \phi_f)^{-1}\tau_p^{-1}$; $k_{dt} = \tau_p^{-1} - k_p$. [c] See note 4. [d] With $\phi_f + \phi_{isc} = 1.0$ assumed. [e] Estimated from 77 K UV absorption spectra.



1

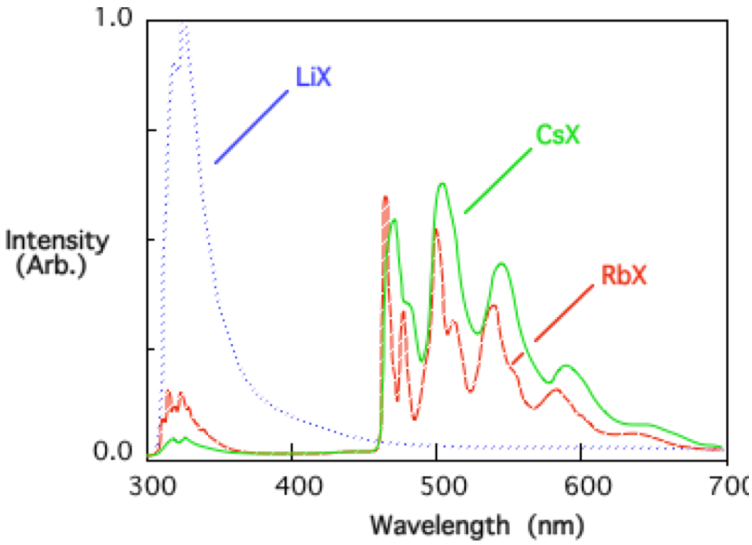
Micelles as hosts

Naphthalene@SDS micelle: effect of heavy atom counterions

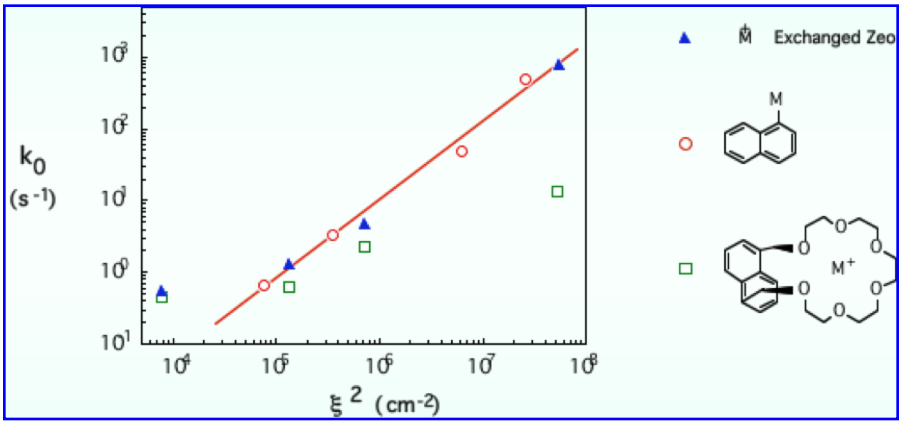


Heavy atom produces more triplets and the triplets produced phosphoresce at a faster rate

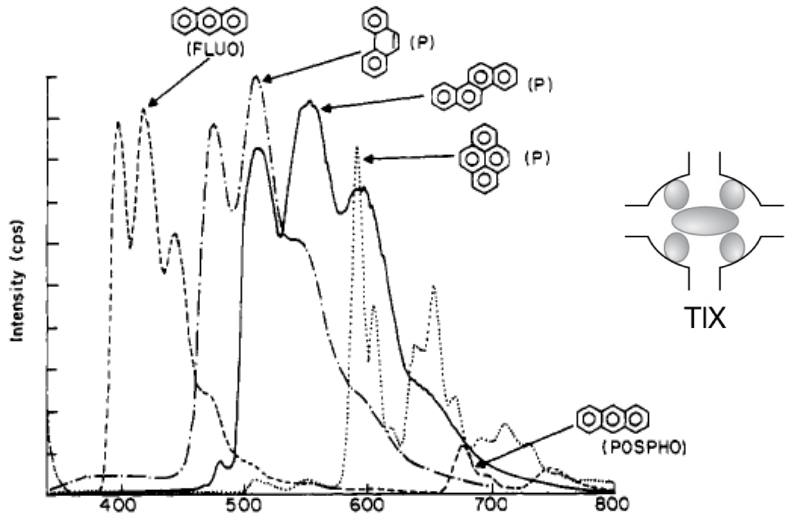
Emission Spectra of Naphthalene Included in MY Zeolites



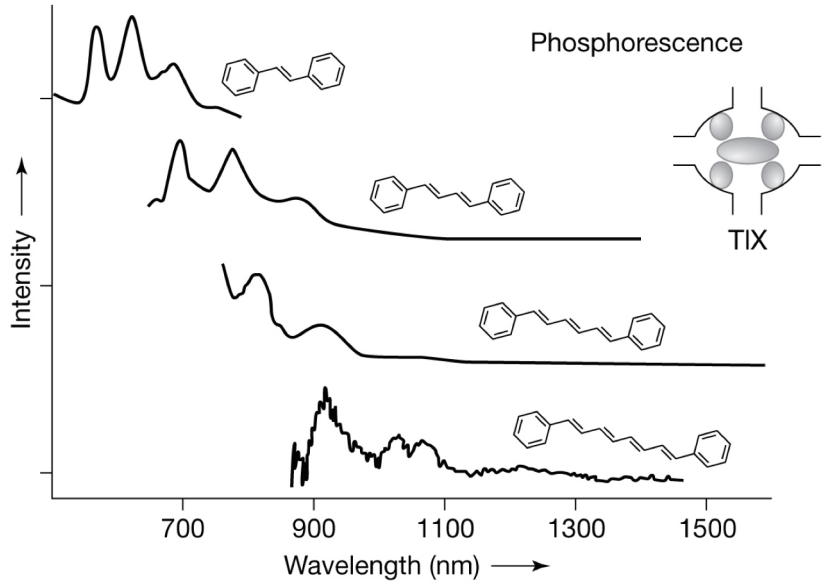
External Heavy Atom Effect on Triplet Decay Rates of Naphthalene



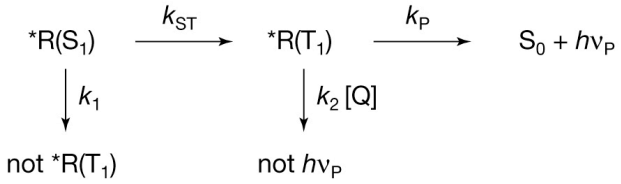
Room temperature phosphorescence

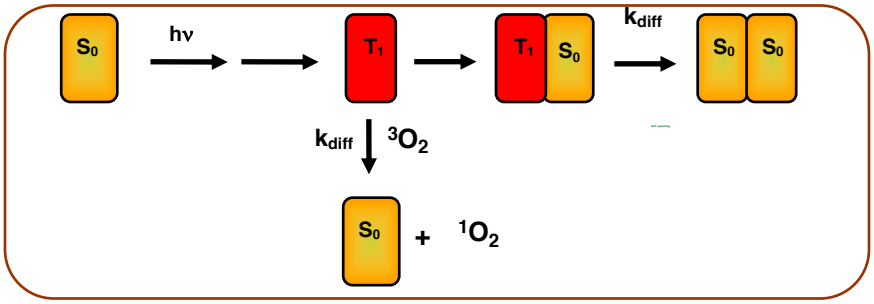


Phosphorescence from Diphenyl Polyenes

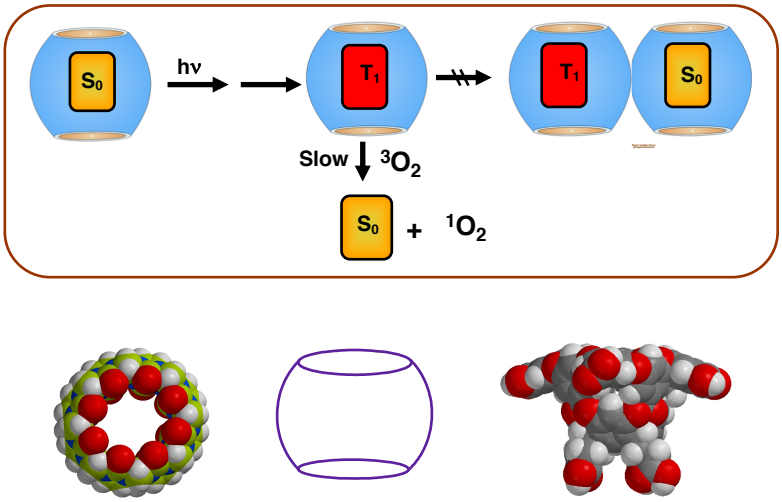


Diffusion controlled self-quenching and oxygen-quenching in solution

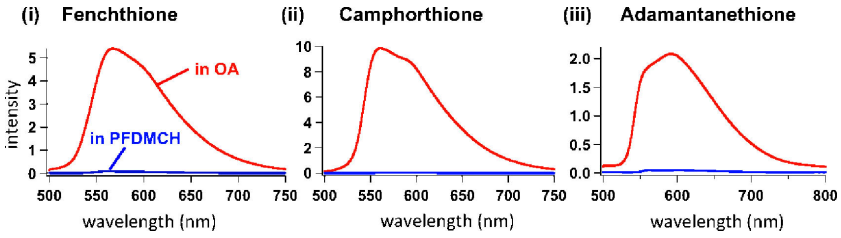


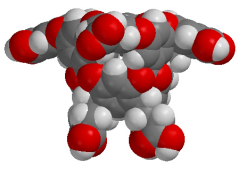


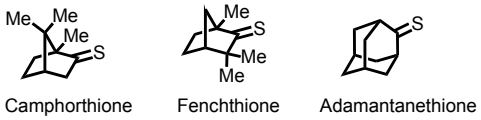
Prevention of self quenching and oxygen quenching with the help of containers

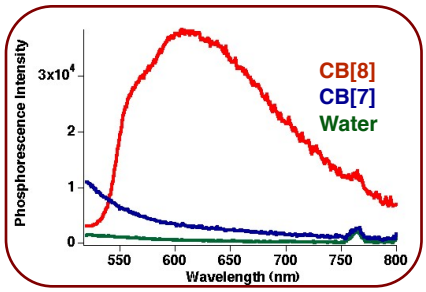


Room temperature phosphorescence from thioketones in solution

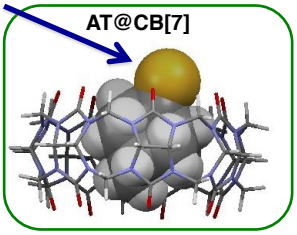




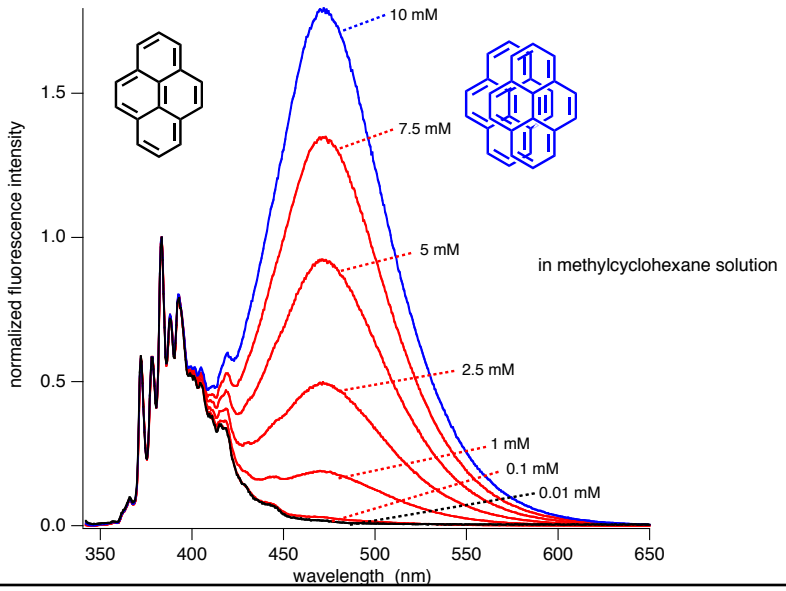




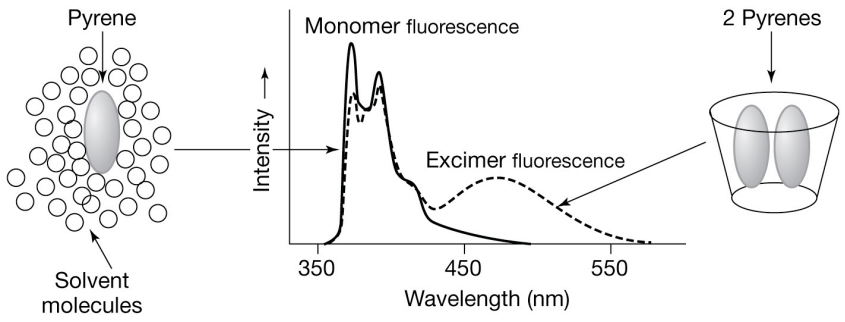
- No phosphorescence in spite of good binding within CB[7] ($K = 4.85 \times 10^4\ M^{-1}$)
- Exposure of C=S to water leads to this anomaly



Pyrene Excimer

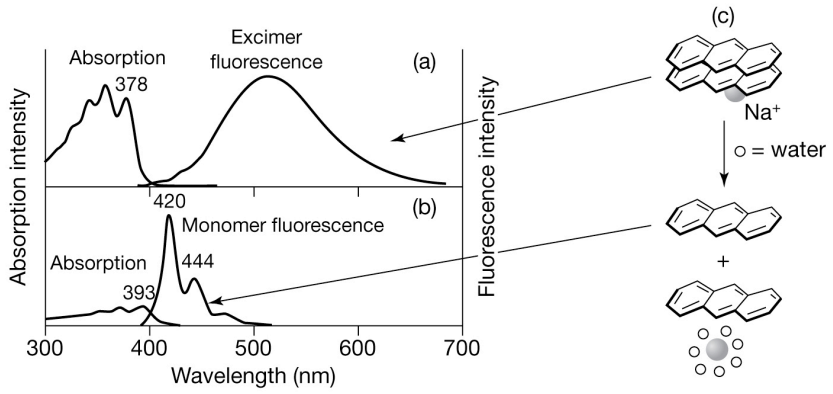


$(Py)_2$@Cyclodextrin: Enhanced excimer formation due to preorganization of two pyrenes in a cyclodextrin cavity

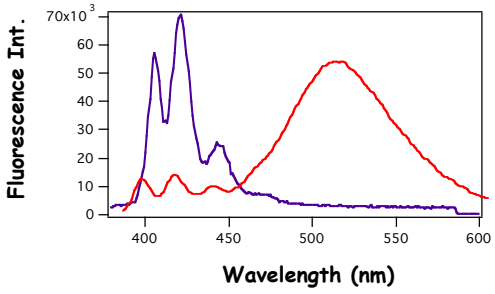


Zeolites as hosts

Anthracene@NaX: Cation controlled aggregation



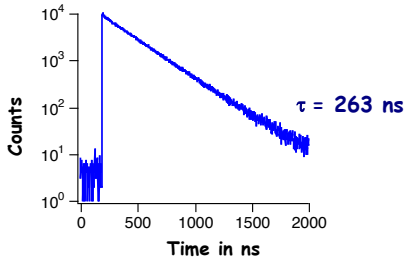
Photophysics of OA-Anthracene Complex

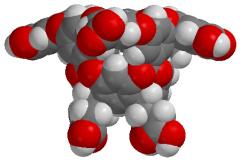


---- Anthracene in water

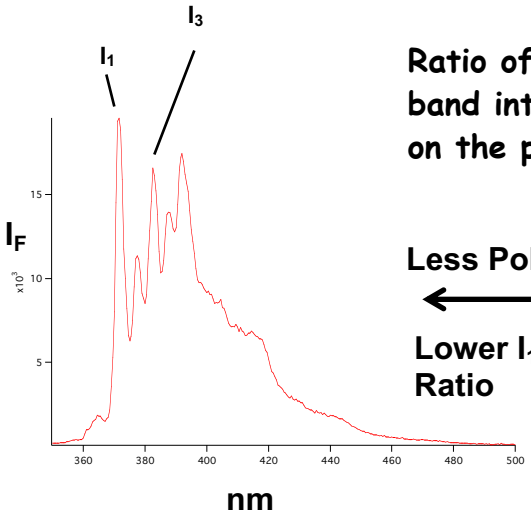
---- Anthracene in octa acid

Sandwich pair emission- slow addition of host to the guest in borate buffer





Fluorescence Response to Solvent Polarities



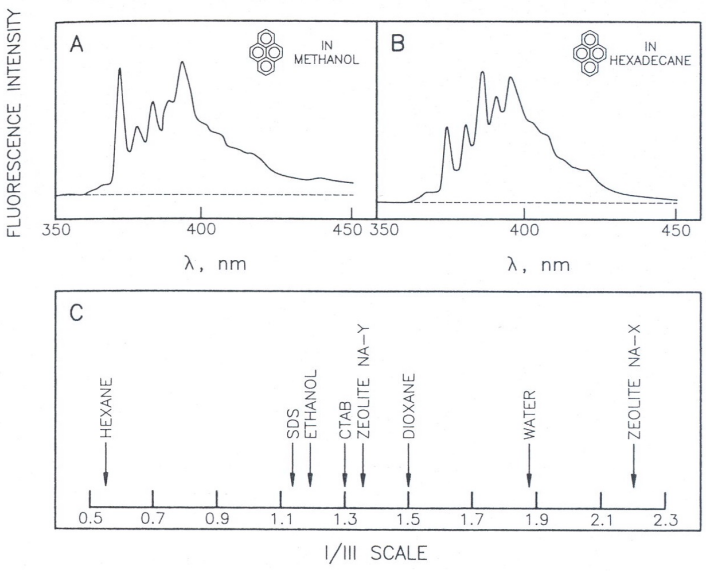
Ratio of 1st to 3rd vibrational band intensities is dependent on the polarity of the solvent.

Less Polar ⟷ More Polar

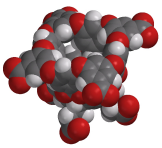
Lower I_1/I_3 Ratio

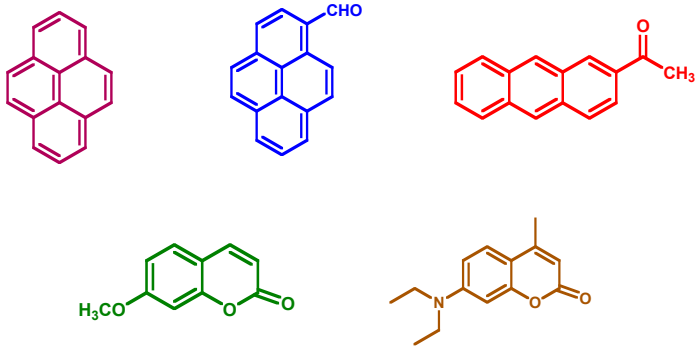
Higher I_1/I_3 Ratio

Pyrene as a polarity probe



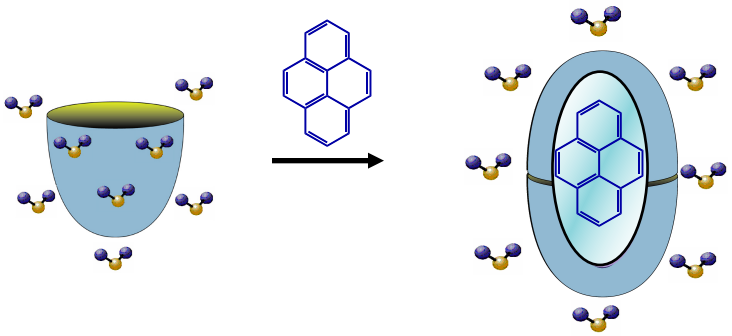
Octa acid's interior micropolarity probed





All above probes form 2:1 host-guest complexes.

Interior of octa acid is benzene-like

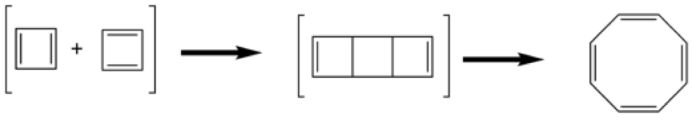


'Dry' and 'Non-polar'

Stabilizing Unstable Molecules

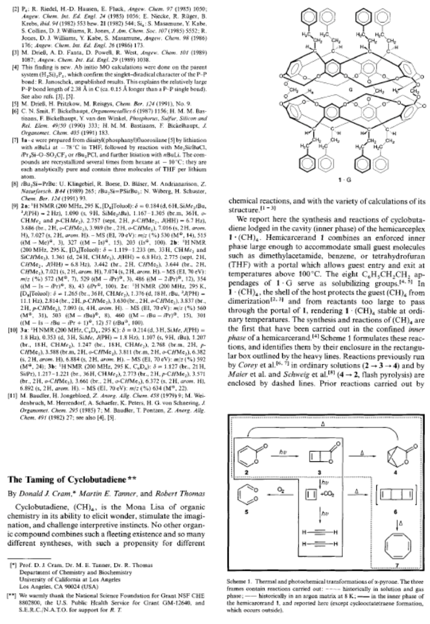
Cram's "taming" of cyclobutadiene

For many years attempts to isolate cyclobutadiene in solution at room temperature failed because one diene undergoes a very rapid Diels-Alder reaction with a second diene molecule (a dimerization)



Cram's idea was to synthesize cyclobutadiene in a host system that would provide supramolecular steric hindrance to prevent dimerization

Cram's breakthrough publication: "The Taming of Cyclobutadiene", Angew. Chem. 30, 1024 (1991)



1 · G

chemical reactions, and with the variety of calculations of its structure.[1–3]

We report here the synthesis and reactions of cyclobutadiene lodged in the cavity (inner phase) of the hemicarceplex **1** · $(CH)_4$. Hemicarcerand **1** combines an enforced inner phase large enough to accommodate small guest molecules such as dimethylacetamide, benzene, or tetrahydrofuran (THF) with a portal which allows guest entry and exit at temperatures above 100 °C. The eight $C_6H_5CH_2CH_2$ appendages of **1** · G serve as solubilizing groups.[4, 5] In **1** · $(CH)_4$, the shell of the host protects the guest $(CH)_4$ from dimerization[2, 3] and from reactants too large to pass through the portal of **1**, rendering **1** · $(CH)_4$ stable at ordinary temperatures. The synthesis and reactions of $(CH)_4$ are the first that have been carried out in the confined *inner phase* of a hemicarcerand.[4] Scheme 1 formulates these reactions, and identifies them by their enclosure in the rectangular box outlined by the heavy lines. Reactions previously run by *Corey* et al.[6, 7] in ordinary solutions (**2** → **3** → **4**) and by *Maier* et al. and *Schweig* et al.[8] (**4** → **2**, flash pyrolysis) are enclosed by dashed lines. Prior reactions carried out by

Scheme 1. Thermal and photochemical transformations of α-pyrone. The three frames contain reactions carried out: ----- historically in solution and gas phase; —— historically in an argon matrix at 8 K; —— in the inner phase of the hemicarcerand 1, and reported here (except cyclooctatetraene formation, which occurs outside).

The Taming of Cyclobutadiene**

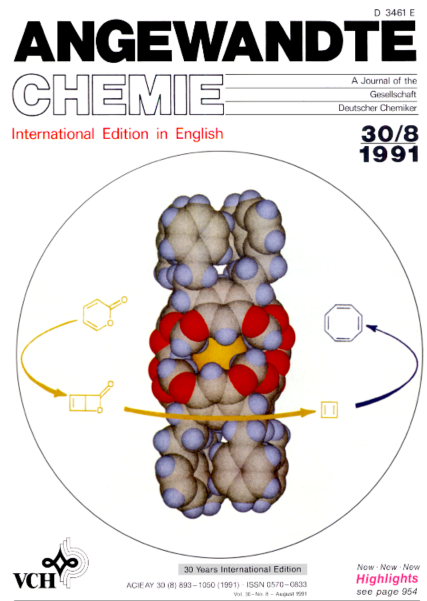
By *Donald J. Cram,* Martin E. Tanner*, and *Robert Thomas*

Cyclobutadiene, $(CH)_4$, is the Mona Lisa of organic chemistry in its ability to elicit wonder, stimulate the imagination, and challenge interpretive instincts. No other organic compound combines such a fleeting existence and so many different syntheses, with such a propensity for different

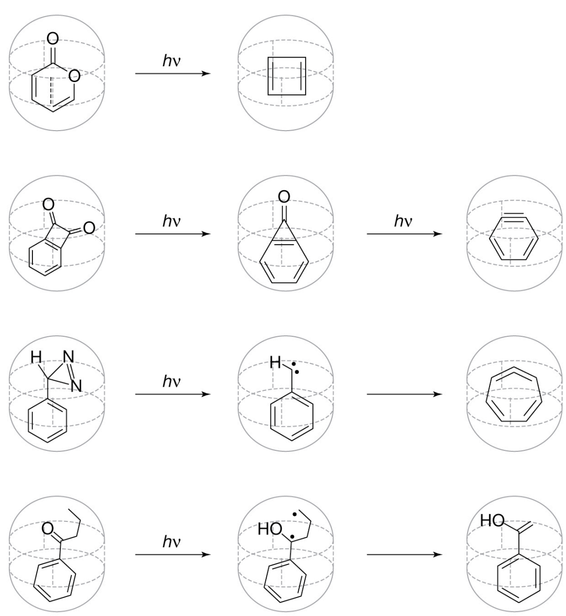
[*] Prof. D. J. Cram, Dr. M. E. Tanner, Dr. R. Thomas
Department of Chemistry and Biochemistry
University of California at Los Angeles
Los Angeles, CA 90024 (USA)

[**] We warmly thank the National Science Foundation for Grant NSF CHE 8802800, the U.S. Public Health Service for Grant GM-12640, and S.E.R.C./N.A.T.O. for support for *R. T.*

1024 © VCH Verlagsgesellschaft mbH, W-6940 Weinheim, 1991 0570-0833/91/0808-1018 $ 3.50+.25/0 Angew. Chem. Int. Ed. Engl. 30 (1991) No. 8



Stabilizing Unstable Molecules



Stabilizing Reactive Intermediates