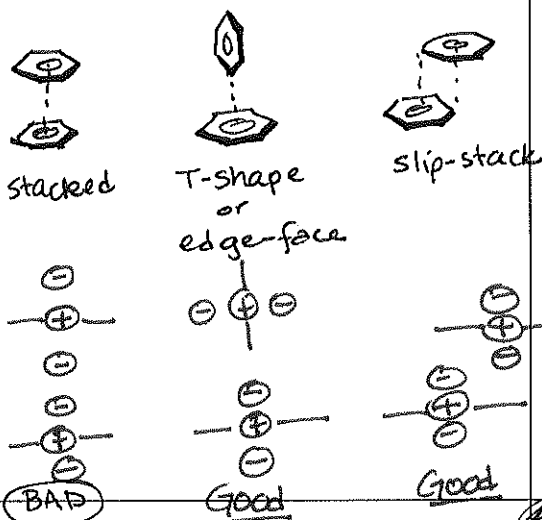


43 π - π interactions

What do these look like?

Possibilities:



Hunter & Saunders
JACS 1990, 1121
5525.
(2300 citations!)

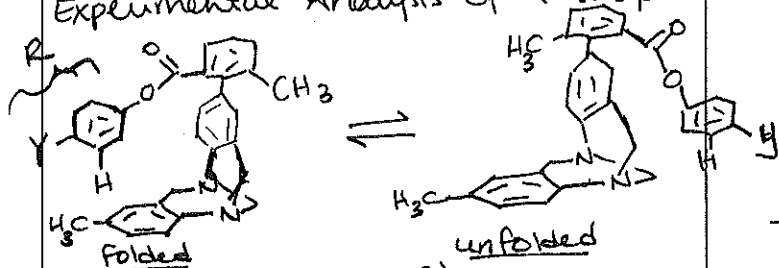
44 Electrostatic Attraction: ~~is~~ +/or Dispersion forces?

Both \rightarrow More electrostatic for T-shape. (Sherill JACS 2004, 126, 7690)

But, computational studies show importance of dispersion component:

Houk JACS 2008, 130, 10854.
Sherill JACS 2009, 131, 4574.

45 Experimental Analysis of T-shape:



Y	% folded (ΔG°)
H	60% (-0.24 kcal/mol)
OMe	60% (-0.24 kcal/mol)
NO ₂	75% (-0.65 kcal/mol)
3,5-dimethyl	35% (+0.37 kcal/mol)
But R = Cyclohexyl	65% (-0.37 kcal/mol)

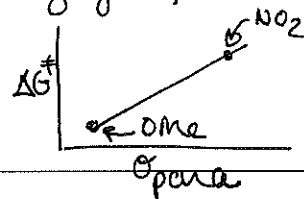
Wilcox
JACS 1994,
116, 4497.

46 Experimental Analysis of Stacked Conformation: X



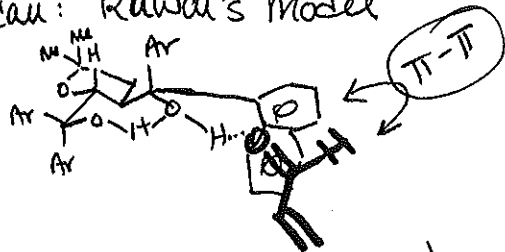
- hindered rotation
- Destabilizing electrostatic interaction
- more destabilizing = faster rotation

Cozzi, Siegel.
JACS 1992,
114, 5729.



47 π - π interactions in organic chemistry

Recall: Rawal's Model



Corey's Model

