

A One-Slide Summary of Quantum Mechanics

Fundamental Postulate:

$$O \Psi = a \Psi$$

operator wave function (scalar) observable

What is Ψ ? *Ψ is an oracle!*

Where does Ψ come from? *Ψ is refined*

Variational Process

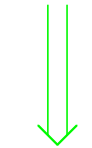
$$\mathcal{H}\Psi = E \Psi$$

Hamiltonian operator (systematically improvable)

Energy (cannot go lower than "true" energy)

electronic road map: systematically improvable by going to higher resolution

convergence of E

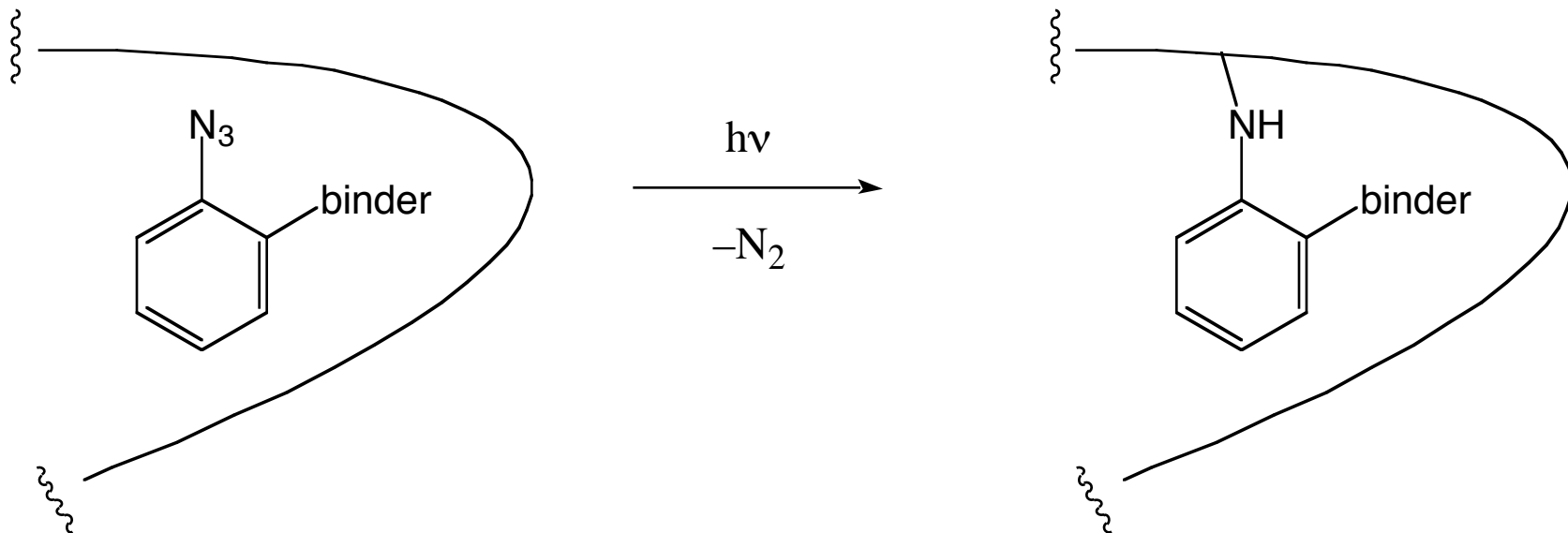


truth

What if I can't converge E ?

Test your oracle with a question to which you already know the right answer...

Photoaffinity Labeling 1



ligand with attached photoaffinity label in enzyme active site

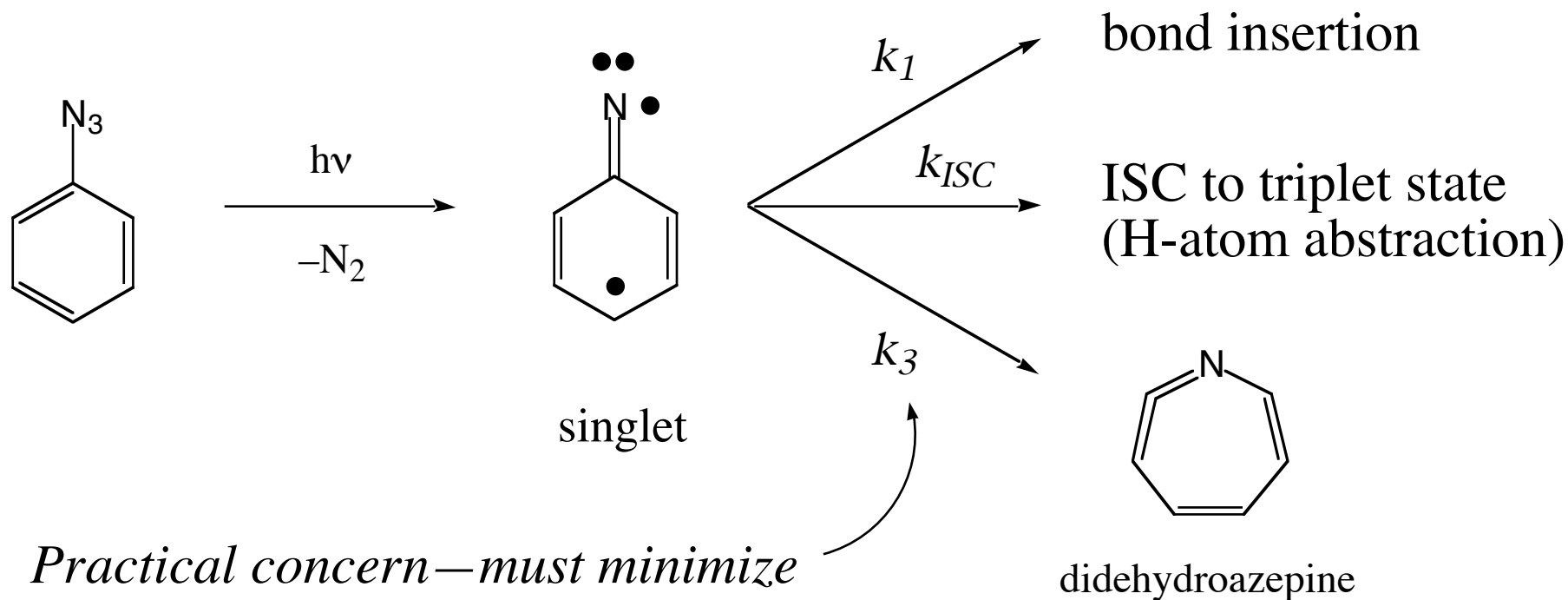
singlet nitrene covalently modifies enzyme – active site can be identified by sequencing of protein

Photoaffinity Labeling 2

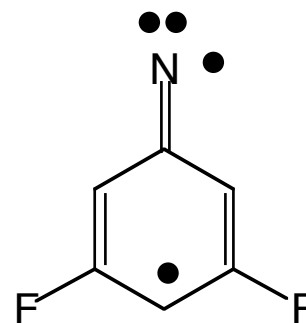
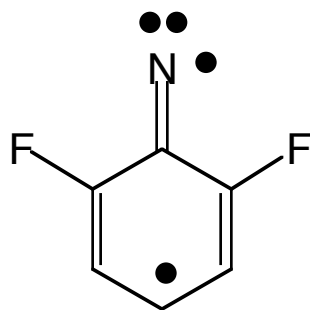
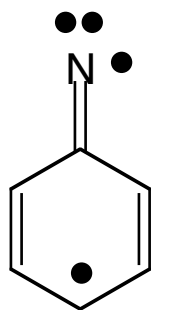
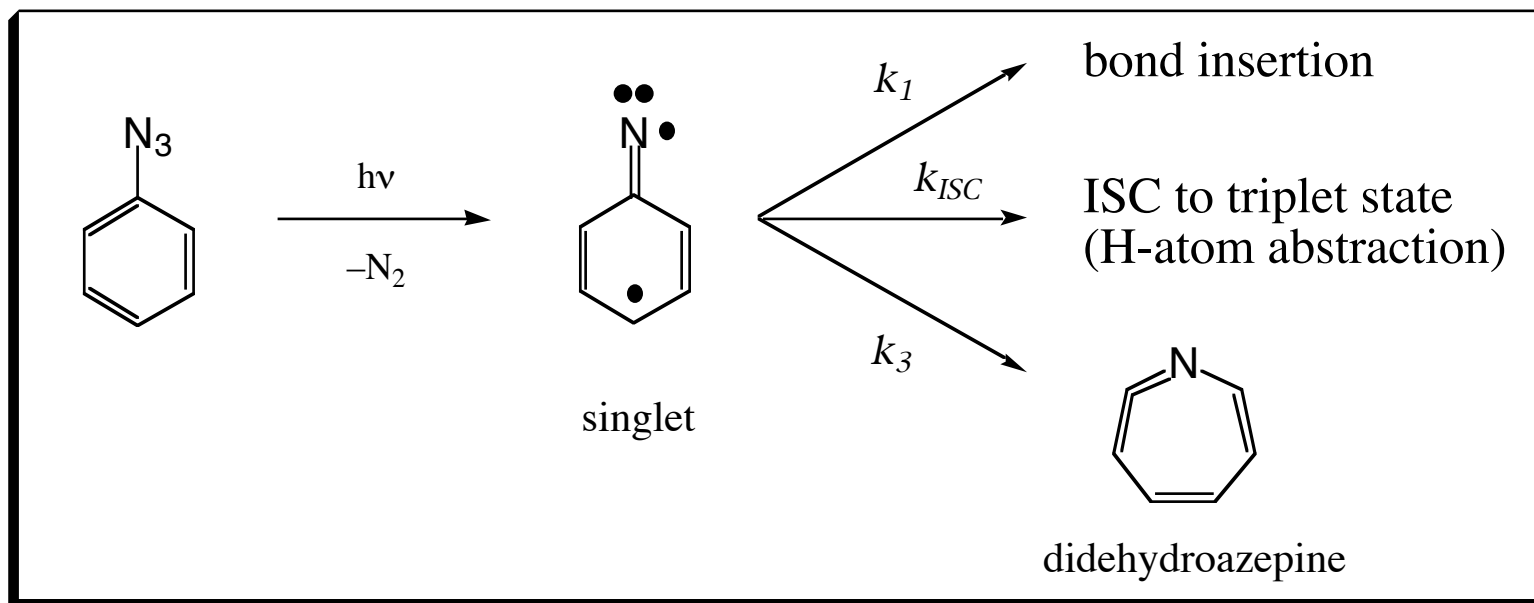
Attractive features of aromatic nitrenes as photoaffinity labels:

- 1) Generated with light outside of protein absorption bands*
- 2) Highly reactive singlets*
- 3) N_2 is an innocuous byproduct of activation*

But:

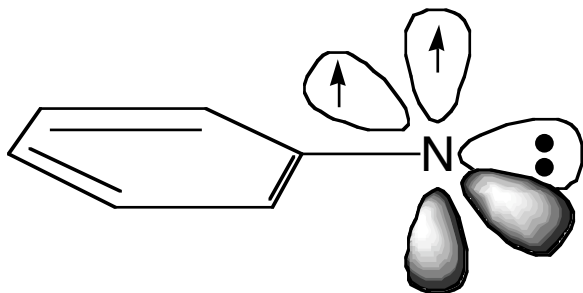


Photoaffinity Labeling 3

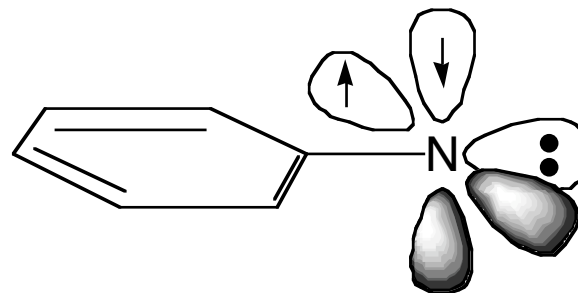


Platz et al.

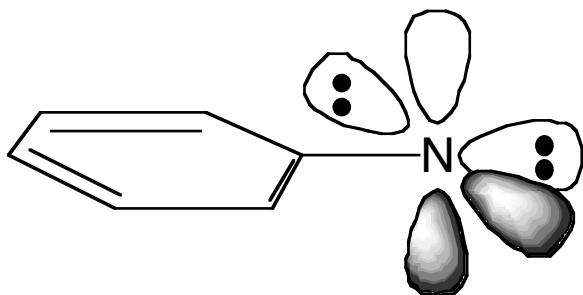
Configuration Cartoons



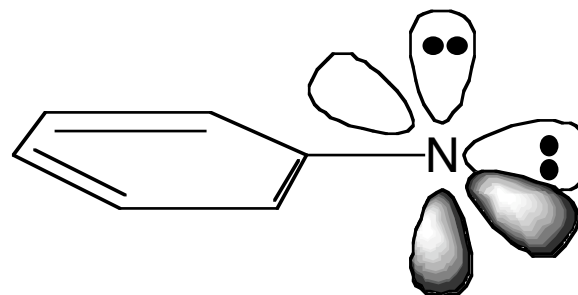
3A_2 (T0)



1A_2 (S1)

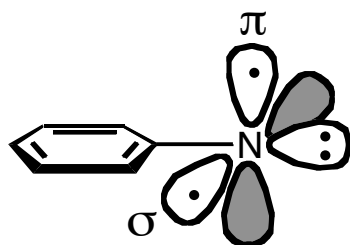


1^1A_1 (S2)



2^1A_1 (S3)

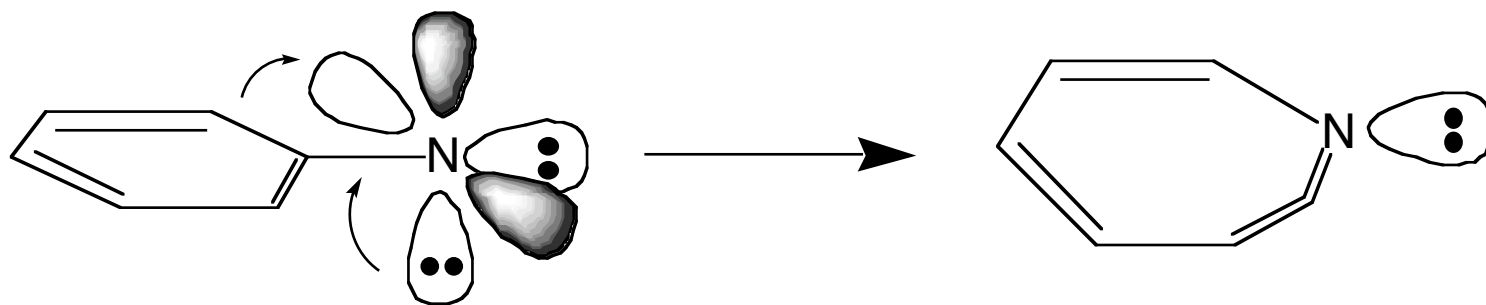
Relative E (kcal/mol) for PhN



	3A_2	1A_2	1^1A_1	2^1A_1
MRCISD/DZP	0.0	21.0	39.8	(52)
CASPT2N(8,8)/TZP	0.0	19.3	34.8	54.5
CCSD(T)/DZP	0.0	—	35.2	(47.2)
BLYP/TZP	0.0	(14.3)	29.5	(41.0)
Expt.	0.0	18	30	?

Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 5349;
 Hrovat, D. A.; Waali, E. E.; Borden, W. T. *ibid.* **1992**, *114*, 8698; Smith, B. A.;
 Cramer, C. J. *ibid.* **1996**, *118*, 5490; Travers, M. J.; Cowles, D. C.; Clifford, E. P.;
 Ellison, G. B. *ibid.* **1992**, *114*, 8699.

Ring Expansion Mechanism

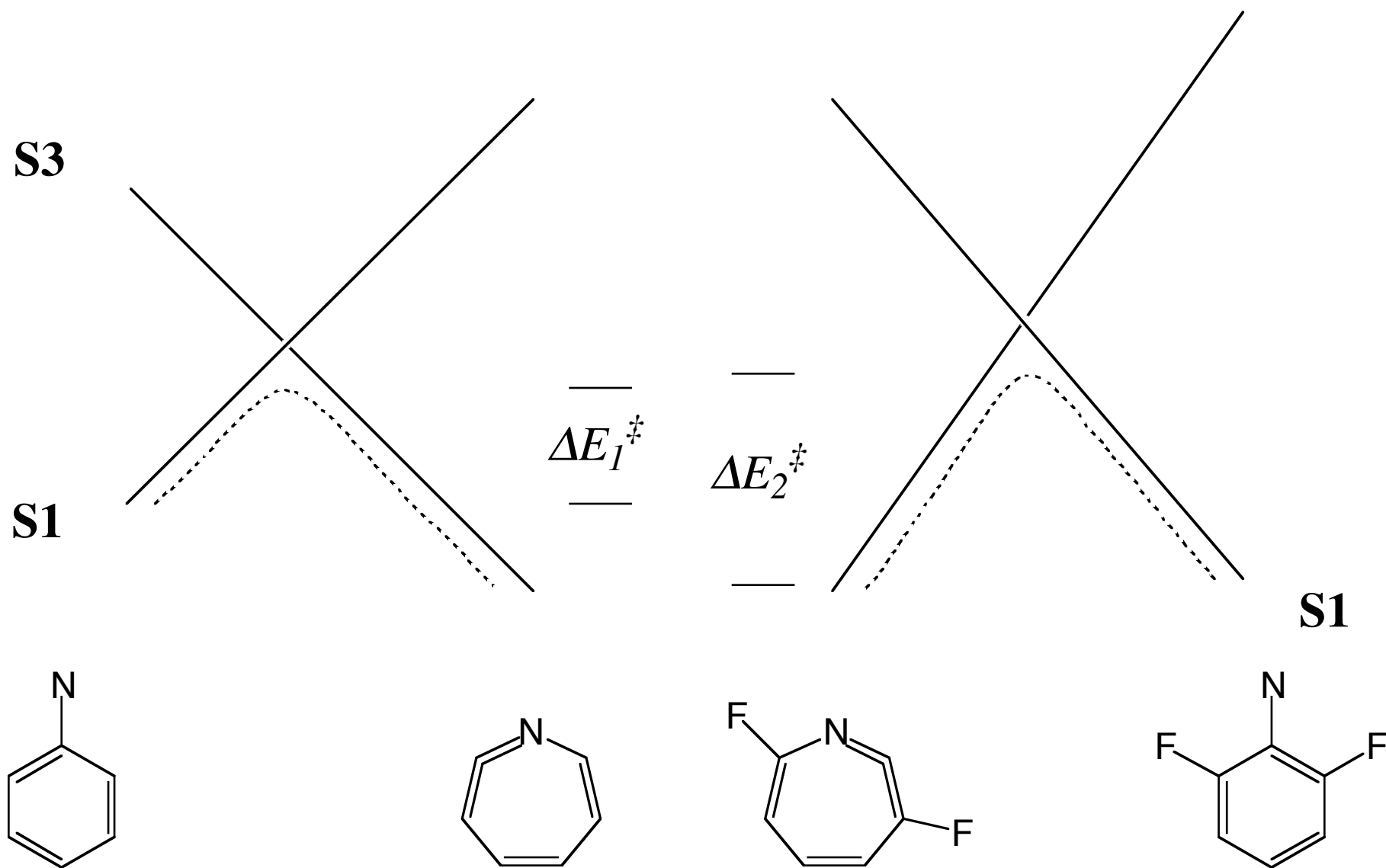


Wagner-Meerwein shift of
CH to aligned in-plane
(empty) N p orbital

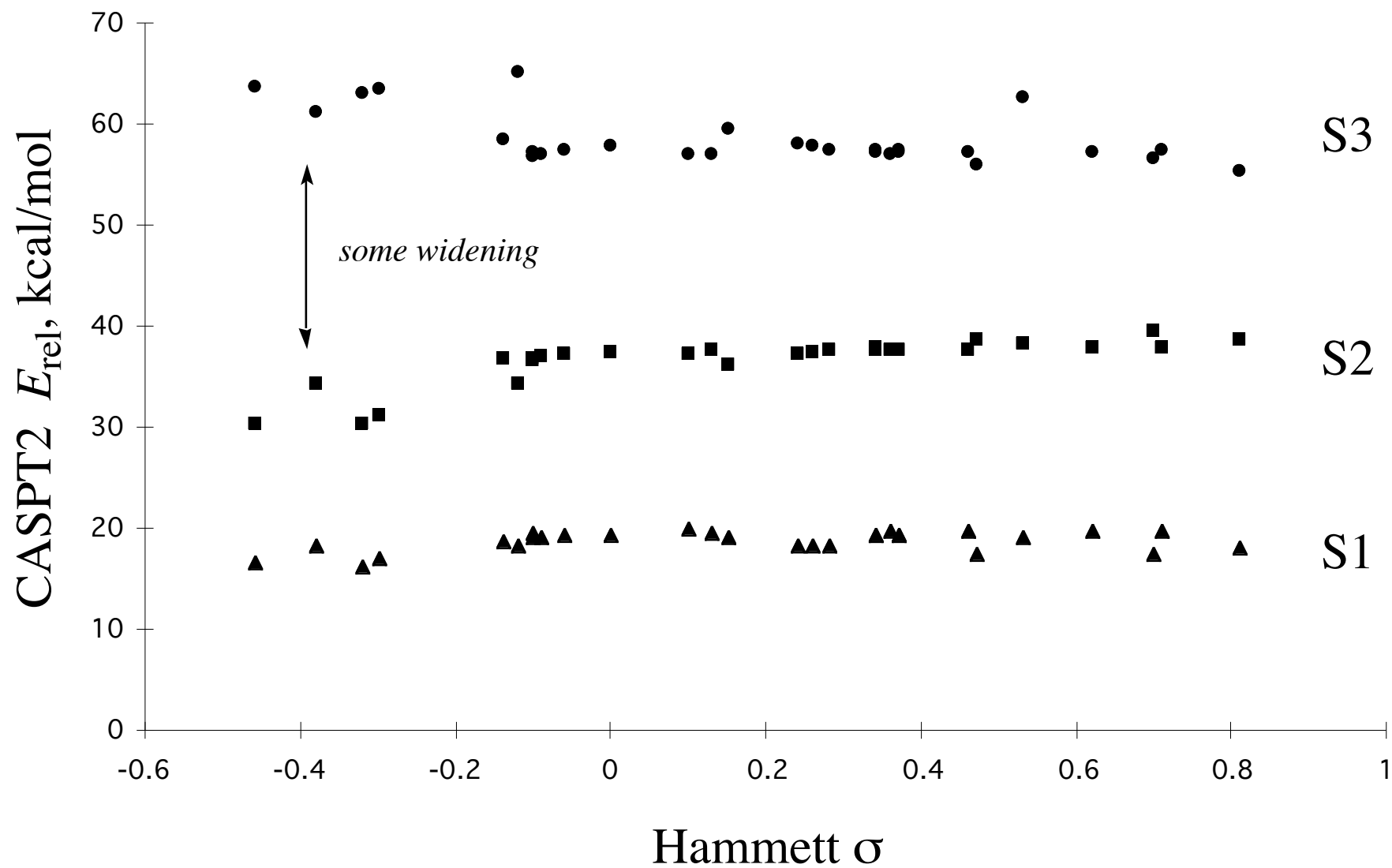
The electronic configuration
of the didehydroazepine
correlates with the S3 nitrene

Avoided Crossing

π -Electron-donating groups should slow ring expansion **S3**



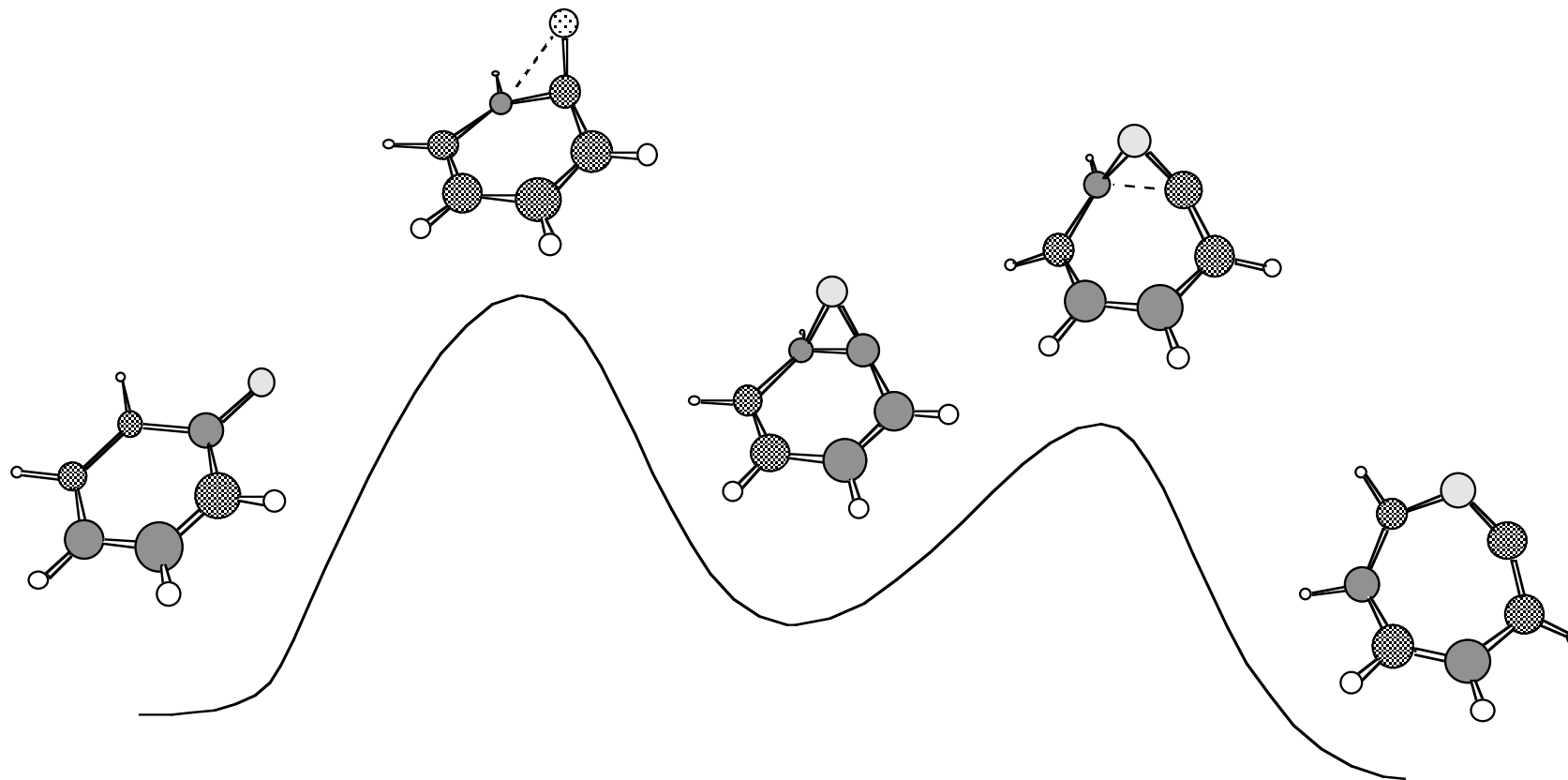
Phenylnitrene Energies With 32 Different *meta* and *para* Substituents



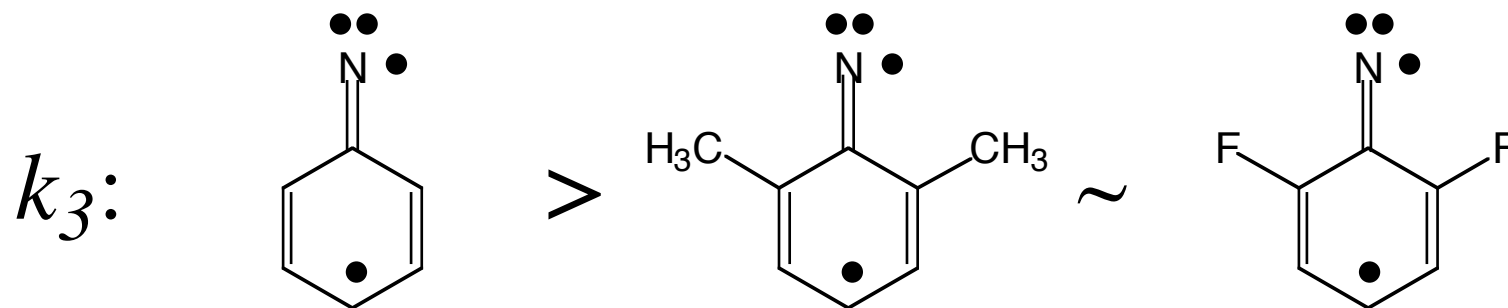
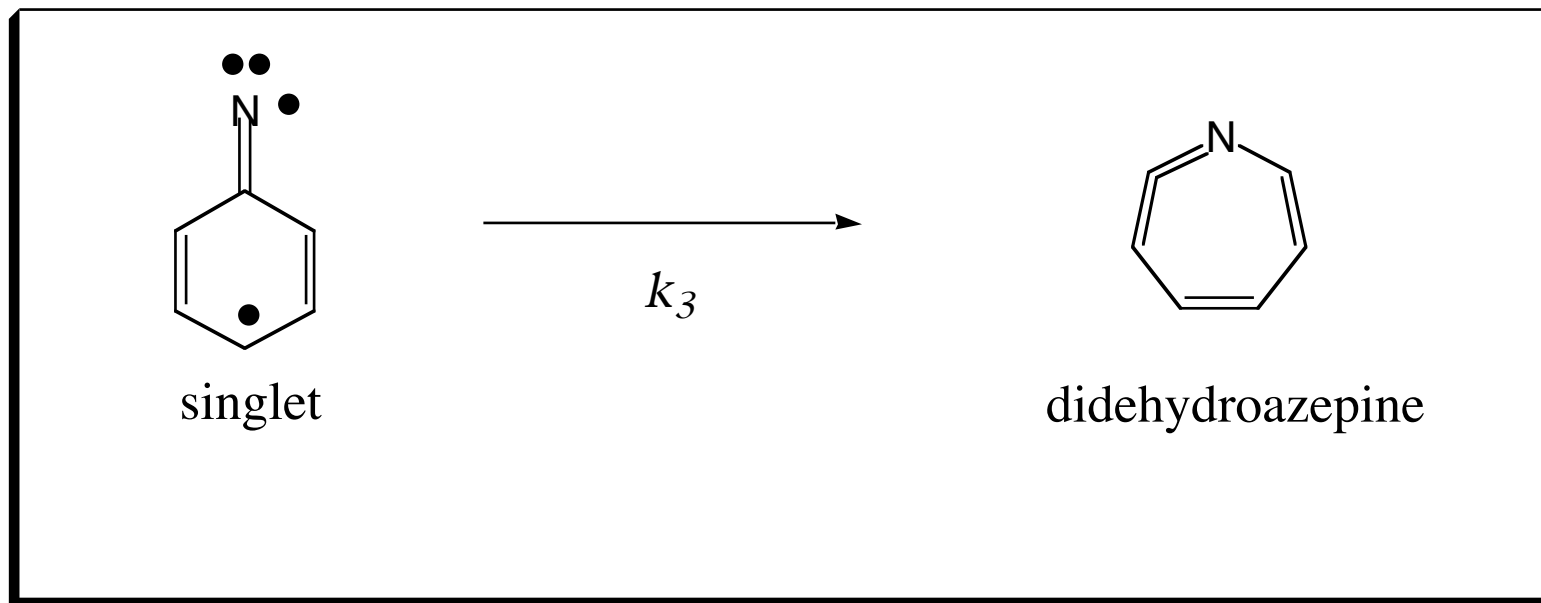
Substituent Effects on Ring Expansion Coordinate

Relative 298 K enthalpies in kcal/mol

NHMe	12.3	8.5	13.3	1.7
H	8.5	2.7	5.8	-1.9
F	8.9	3.0	7.3	-1.6
NO₂	9.5	3.7	4.8	-0.7



Photoaffinity Labeling 4

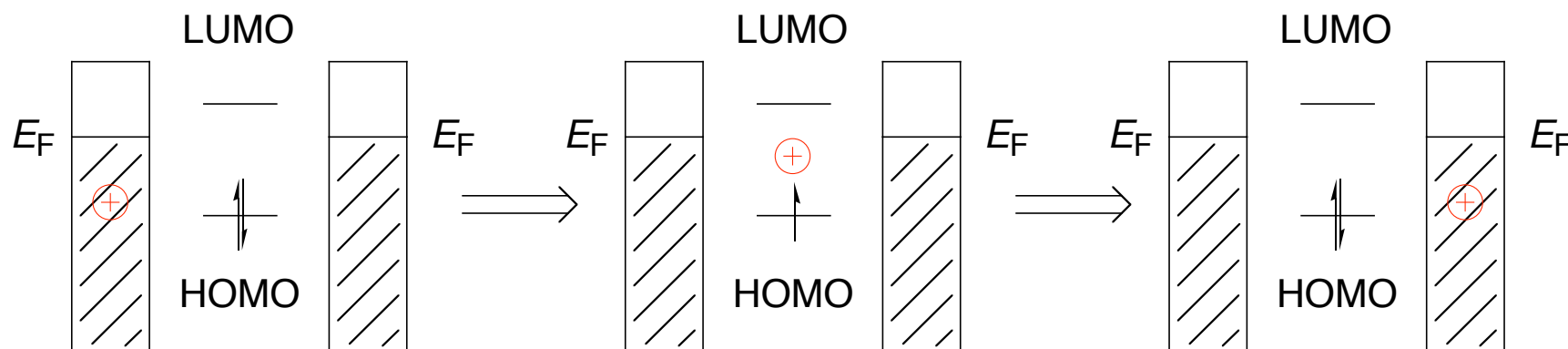
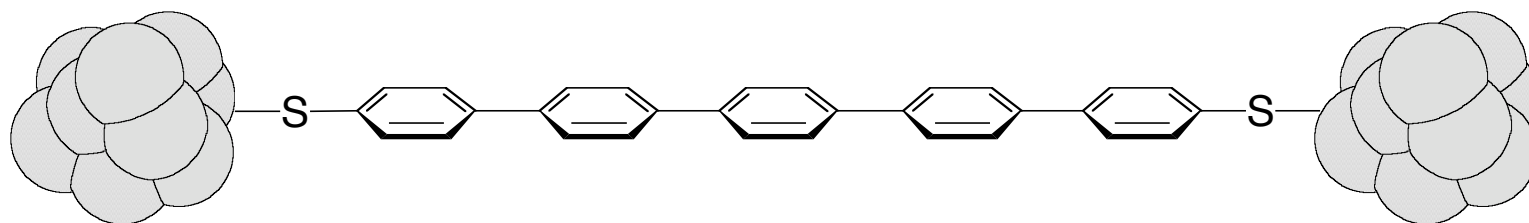


Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347.

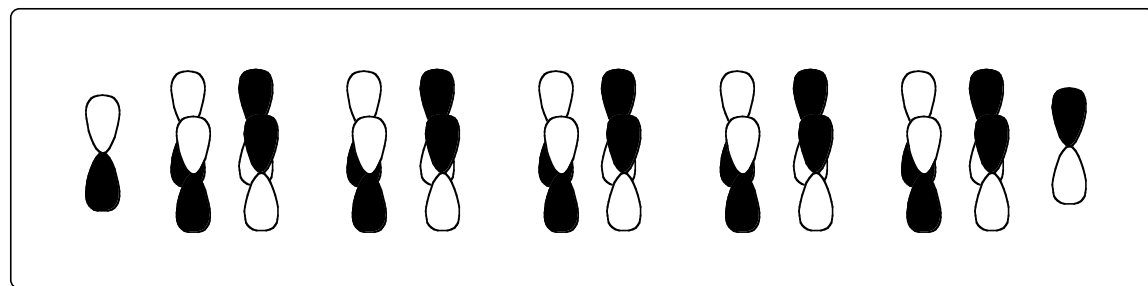
Theoretical Recommendation

Optimal photoaffinity labels will be aromatic azides combining steric bulk at *ortho* positions with strong electron-donating group at *para* position

Molecular Wires — Hole Transport

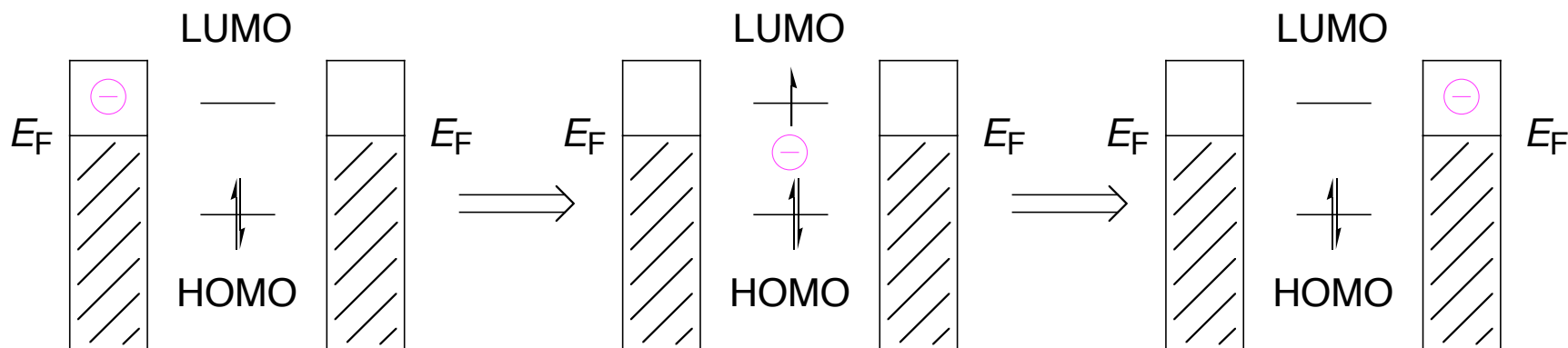
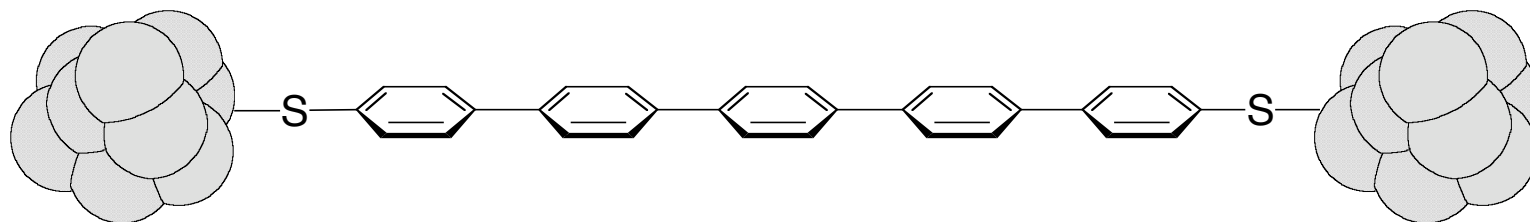


*Generally good conduction
because of significant overlap
between HOMO of organic
wire and filled metallic bands*



HOMO

Molecular Wires — Electron Transport



Less well characterized—what do the virtual orbitals of the organic wire look like?

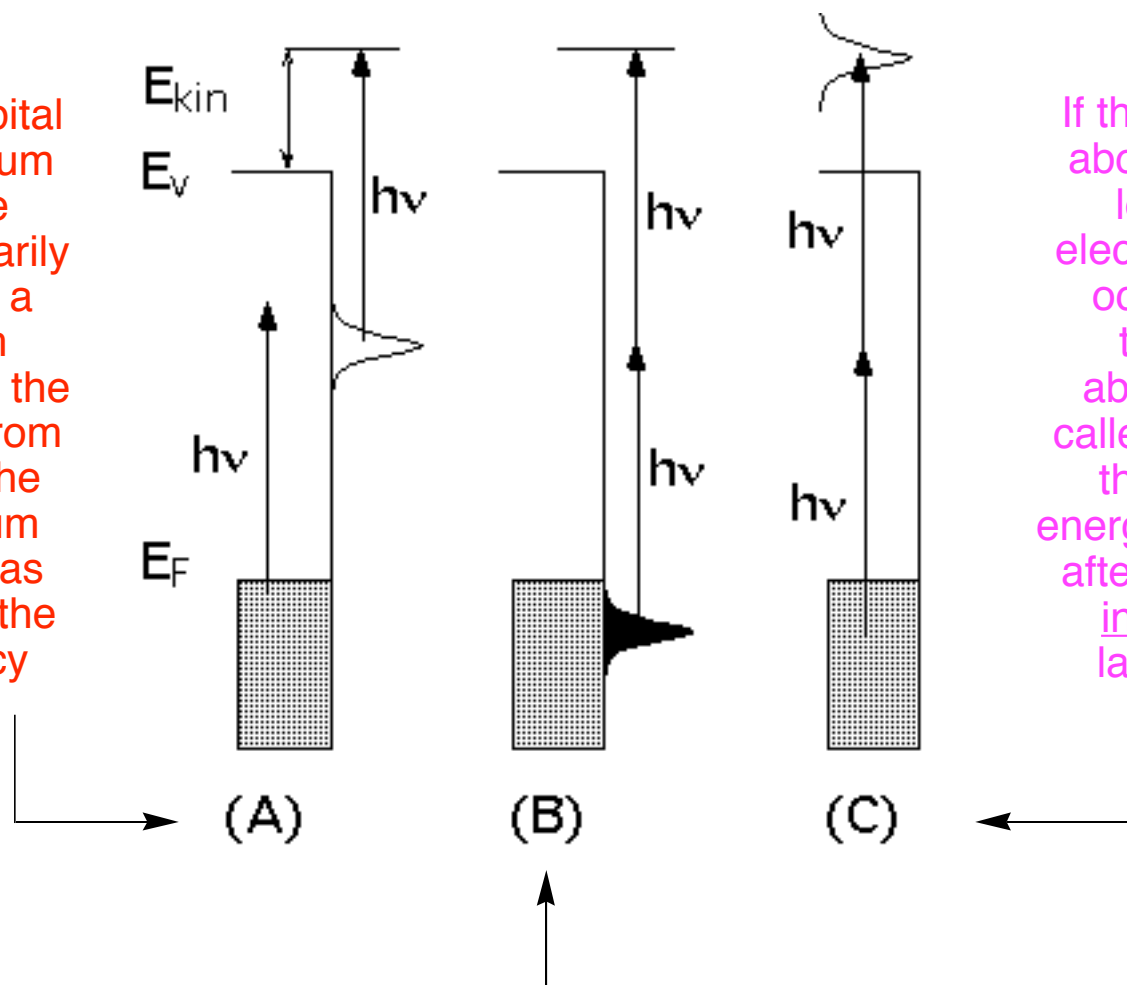
?

LUMO

Experimental Method to Characterize Virtual Orbitals

Two-photon photoelectron spectroscopy (2PPE)

If there is an orbital below the vacuum level, that the electron temporarily occupies after a one-quantum absorption, then the kinetic energy from absorption of the second quantum scales exactly as the increase in the laser frequency



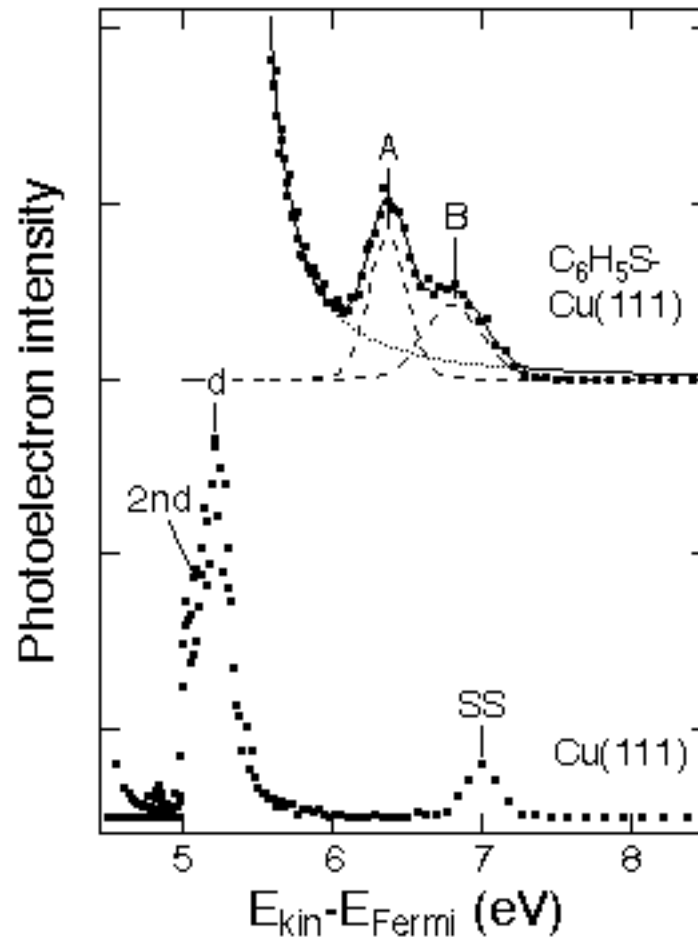
If there is an orbital above the vacuum level, that the electron temporarily occupies after a two-quantum absorption (a so-called "resonance"), then the kinetic energy of the electron after detachment is independent of laser frequency

If the excitation involves a direct two quantum absorption, the kinetic energy of the detected photoelectrons increases as twice the increase in laser frequency

2PPE Example: Phenylthiolate on Copper

3.7 eV Photons

After covering the surface with an organic monolayer, a copper surface state disappears, and two new peaks are observed

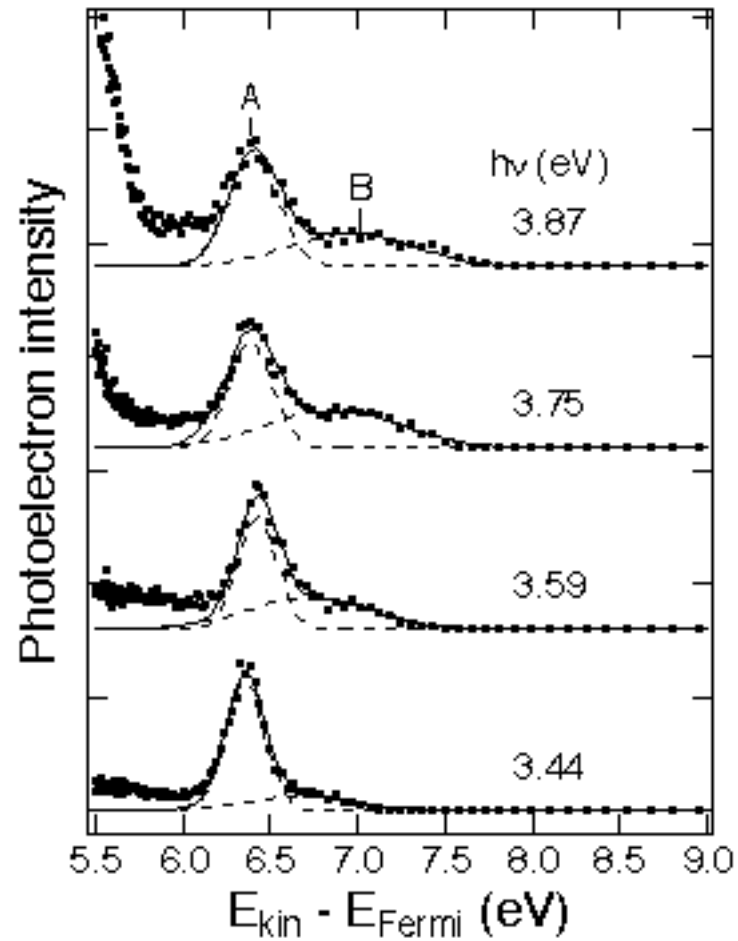


covered surface

clean surface

Phenylthiolate on Copper: Effect of Altered Photon Energies

Peak B moves,
but Peak A
does not



Peak Positions as a Function of Photon Energies

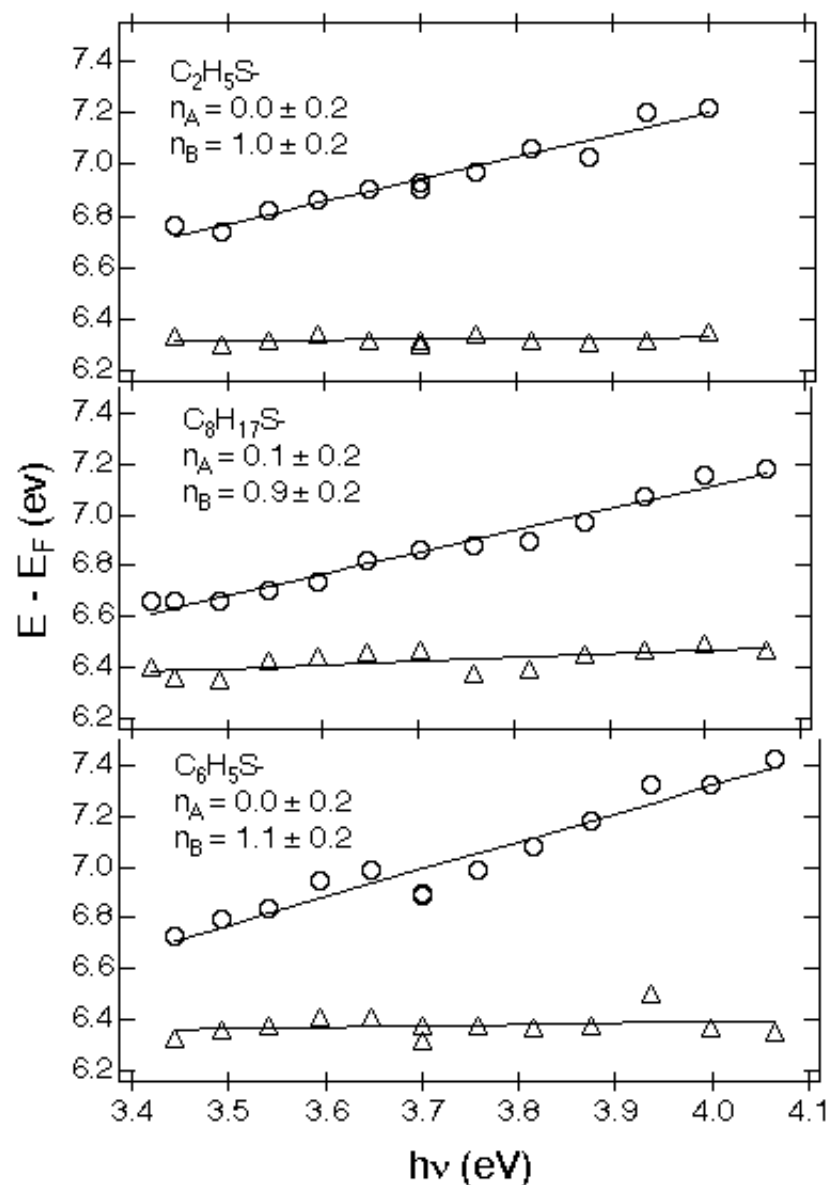
The spectra are essentially identical for three different thiolate coverages:

A corresponds to a resonance above the vacuum level (slope = 0)

B corresponds to a virtual orbital below the vacuum level (slope = 1)

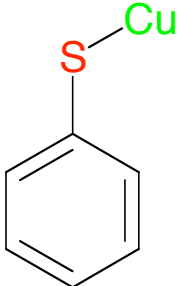

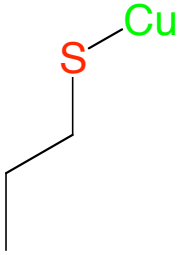

What orbitals would be unaffected by the change of phenyl to ethyl to octyl?

Notice that the point of intersection of the two lines corresponds to the energy difference between the virtual orbitals (3,1 eV)

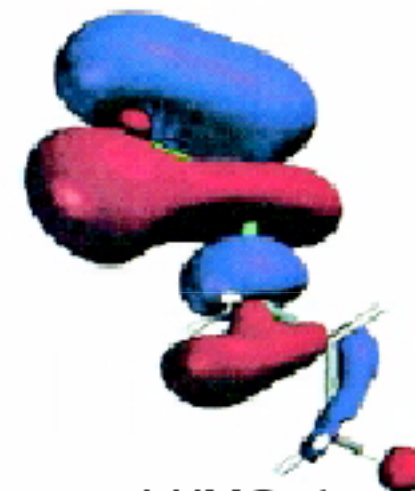
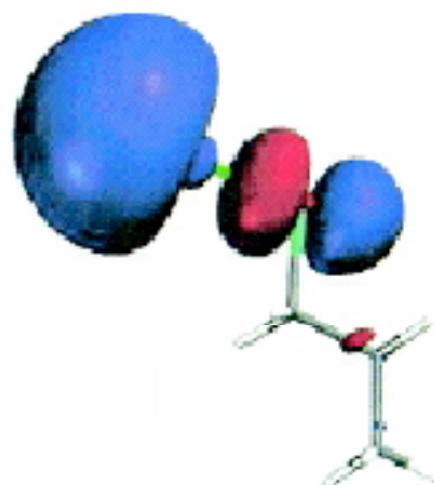
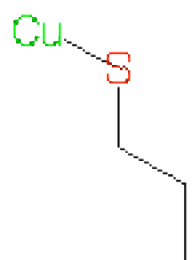
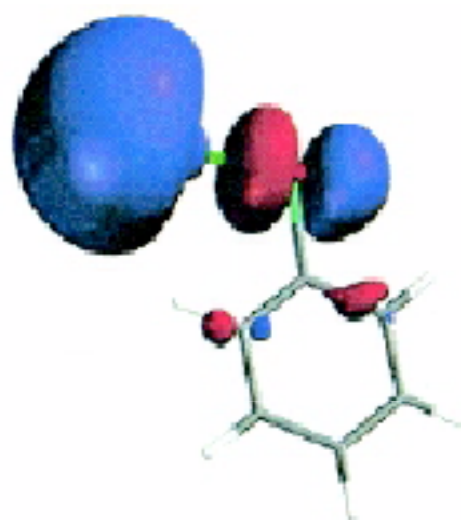
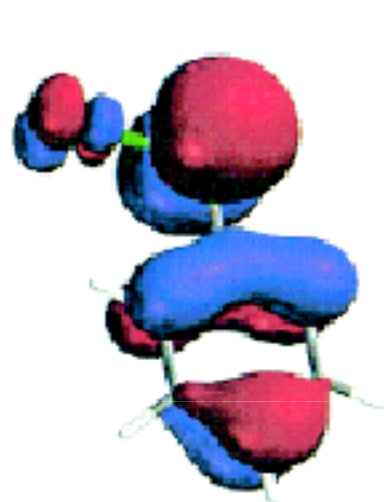
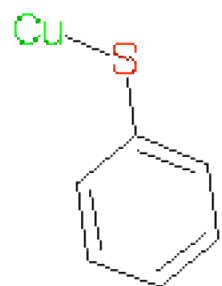


Computed Properties of Phenyl- and Propylthiolate

B3LYP/pVDZ+, units of eV, vertical properties

	$1^2A''^+ \leftarrow 1^1A'$ Ionization Potential	$1^2A'^- \leftarrow 1^1A'$ -Electron Affinity	$2^2A'^- \leftarrow 1^1A'$
	7,3	-1,3	1,1
		 ~ 2,4	
	7,9	-1,0	1,3
			
	-HOMO Δ SCF	+LUMO Δ SCF	+LUMO+1 Δ SCF _{LUMO} + Δ ϵ _{LUMO/LUMO+1}

Orbitales de Fenil- y Propiltiolato de Cálculo



son similarísimo

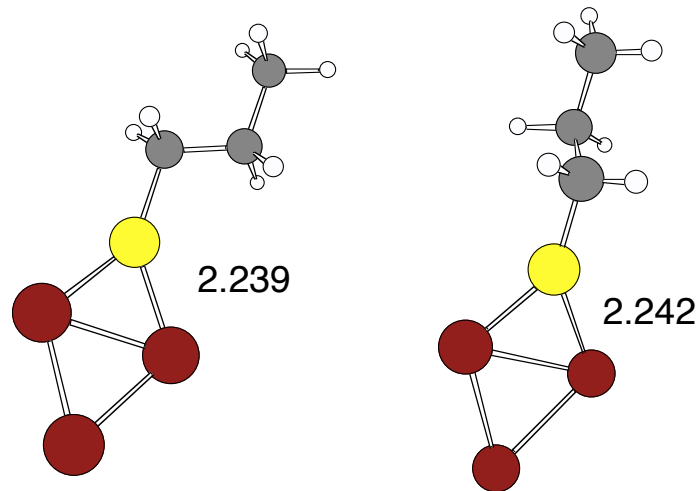
HOMO
simetría- π

LUMO
 σ^* CuS

LUMO+1
 σ^* CS

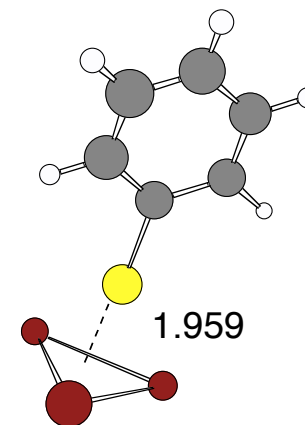
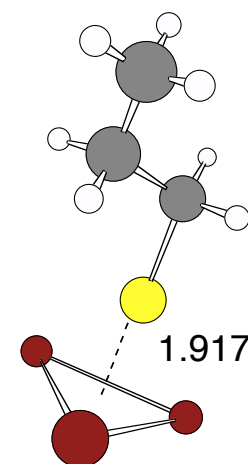
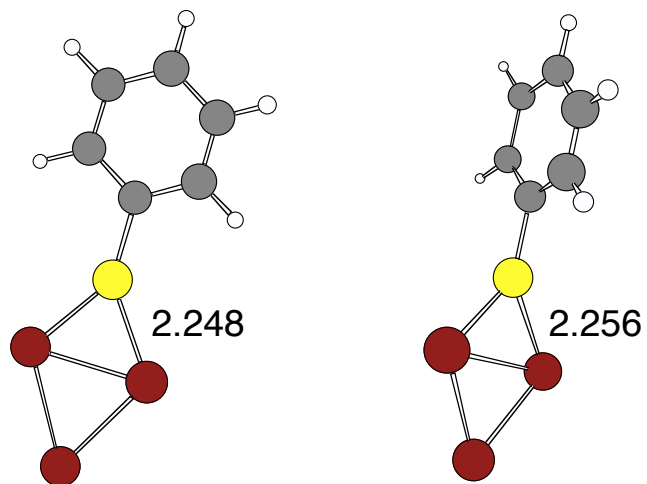
Improving the Surface Model

Little energetic difference between the two stereoisomers



The important orbitals are qualitatively the same as for the case with only one copper

The differences between LUMO and LUMO+1 in the two systems are 2.9 and 3.1 eV—in perfect accord with experiment (3.1 eV)



$\sim 15 \text{ kcal mol}^{-1}$
higher in energy

Conclusions

1. The orbitals observed in the 2PPE experiment are the LUMO and LUMO+1 (σ^*_{CuS} and σ^*_{CS}) of the thiolate. These orbitals are below and above the vacuum level, respectively, and are qualitatively independent of the thiolate R group.
2. In addition, these orbitals fail to delocalize significantly off the Cu–S–C fragment. Thus, one assumes they will not facilitate conduction across an organic chain. This contrasts with the situation for the HOMO (used in hole transport) which *is* well delocalized.
3. Thiolates prefer to coordinate between two atoms of copper (side-on) rather than face on to a triangle of three surface atoms. The characters of the virtual orbitals localized on the organic fragment are not much affected by the presence of additional metal atoms.

Final Exam

- 10:30 to 12:30 Wednesday, May 10
- A–L 375 Science Classroom Bldg
M–Z 331 Smith Hall
- CJC Office Hours today 2-3 PM 221
Smith Hall