

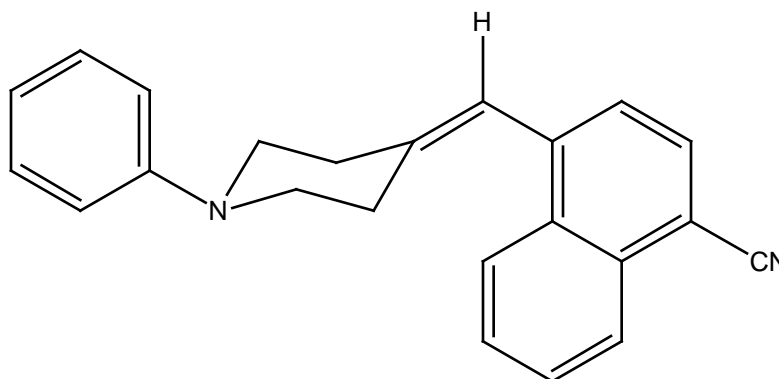
## Chemistry 416, Dr. Glaser

### Solvent Effects on UV/Vis Spectra: Fluorescence of an ICT System.

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An extreme example of solvent-dependent fluorescence of an ICT excited state molecule is shown by 1-phenyl-4-(4-cyano-1-naphthylmethylene)piperidine, a bichromophoric molecule with a donor D and an acceptor A separated by an elongated spacer. The absorption spectrum is nearly independent of the solvent polarity and resembles the sum of the independent spectra of the D and A chromophores. What excitations are these? Why are they almost solvent-independent?

In the fluorescence spectrum there is just one emission and it undergoes a dramatic shift with solvent polarity. This behavior is characteristic of a highly dipolar or zwitterionic ICT excited-state molecule. The dipole molecule in the ICT complex is 25 D (the ground state dipole moment is 1.6 D)! Suggest a structure for the ICT complex.



Solvent	n-hexane	benzene	CHCl <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>
max(fluor.) [nm]	412	478	531	579
Solvent	pyridine	CH <sub>3</sub> CN		
max(fluor.) [nm]	627	694	+282	