**Chemistry 552** **Spectroscopy** **Fall 2003**

Name:__________KEY__________________________

(1) (10 pts) The ultraviolet spectrum of benzonitrile shows a primary absorption band at 224 nm and a secondary band at 271 nm. The spectrum is obtained in a 1 cm pathlength cuvette.

- (a) a solution of benzonitrile in water with a 0.1 mmolar concentration is examined at a wavelength of 224 nm. The absorbance is determined to be A = 1.30 What is the molar absorptivity of this band
- (b) if the same solution is examined at 271 nm, what will be the absorbance reading, assuming that ε = 1000 for this band?

Remember that $A = \varepsilon \ell c = abc$; let ε and *a* be molar absorptivity, $\ell$ and *b* path length, *c* concentration; the two equations are typically used as being equivalent, so we will do the same.

A = 1.30 = (ε) × (1 cm [a standard path length]) × (0.0001 moles/liter)

Rearranging, we find that ε = 13000 L/mol-cm

(units of ε are often ignored, but must cancel the units of pathlength and concentration, since A is a logarithmic function and hence unitless).

If ε(271 nm) = 1000 L/mol-cm, then the ratio

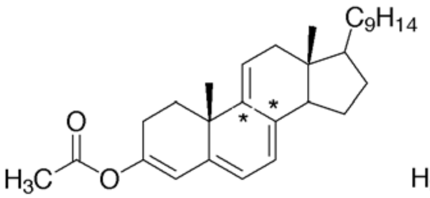
A(λ = 224 nm) / A(λ = 271 nm) = ε(224 nm) / ε(271 nm)

1.30 / A(λ = 271 nm) = 13000 / 1000

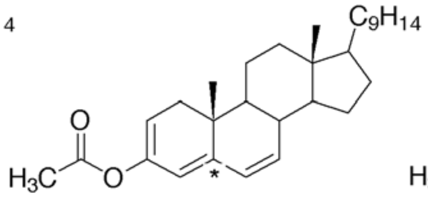
Rearranging, we find that A(λ = 271 nm) = 0.10

The band at 224 nm is a benzene ring $\pi \rightarrow \pi^*$ transition, consistent with the large molar absorptivity. The longer wavelength band is also likely a $\pi \rightarrow \pi^*$ transition, somewhat affected by conjugation to the cyano group, and with a weaker intrinsic absorptivity. This is typical of benzene-based UV-vis spectra, to have a shorter wavelength strong $\pi \rightarrow \pi^*$ transition, and a longer wavelength set of weaker $\pi \rightarrow \pi^*$ transitions.

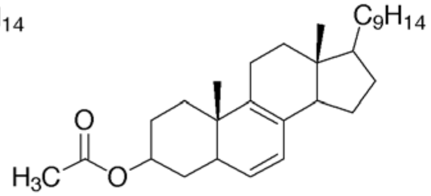
(2) (10 pts) Match the steroid structures shown below to the following values of the UV-vis band maximum in hexane: A = 275 nm, B = 304 nm, C = 356 nm. Use both qualitative arguments, Woodward's rule predictions, and/or specific comparison spectral information that you have available. If you cite comparison spectra, you must give your literature reference or WWW URL.



C



B



A

The assignment given above is pretty straightforward in qualitative terms. There is no cross conjugation here, only straight, linear conjugation. The left-most molecule has four conjugated C=C, the middle has three, the right-most has only two. The longest conjugated system should have the longest wavelength UV-vis transition. The asterisks show exocyclic double bands, as explained for B and C below.

**For A**

http://webbook.nist.gov/cgi/cbook.cgi?ID=C106990&Units=SI&Mask=200#UV-Vis-Spec
shows butadiene with an absorption max of about 290 nm, but this is a fairly weak band.
The main absorption of butadiene is at about 217 nm, much shorter than any of these. The main absorption of 1,3-cyclohexadiene, however, is about 256 nm, a decent match for A even without doing the Woodward analysis. This is because of the rigidity and conformational similarity of A to cyclohexadiene.

By Woodward analysis, this is a homoannular diene, base = 253 nm (see your handouts on UV-vis). There are four alkyl substituents off the conjugated system, each worth an increment of +5 nm. The predicted UV-vis maximum is at 273 nm, very close to the observed 275 nm value!

**For B**

http://www.lhup.edu/~rkleinma/Chem430/Practice/problems2.htm
1,3,5-hexatriene has a main absorption at about 253-263 nm, which is shorter wavelength than B. The rigid geometry of B gives better net conjugation, and a longer wavelength maximum.

By Woodward analysis, this is a homoannular diene, base = 253 nm. The conjugation length is extended by one C=C, for an increment of +30 nm. There are three alkyl substituents off the conjugated framework, each worth +5 nm. There is one OAc group in the conjugated framework, worth +0 nm. One adds an increment of +5 nm for each "exocyclic C=C", meaning a C=C that is can be considered as attached to the vertex of a ring (see the * positions above) – there is one in B. The predicted UV-vis maximum is at 303 nm, quite close to observed 304 nm.
If you use a heteroannular diene base of 214 nm, with conjugation extension of +30 nm, three alkyl substituents, and one exocyclic C=C, you predict 265 nm, well below any of the observed values. The homoannular base overrules the higher energy, heteroannular base.

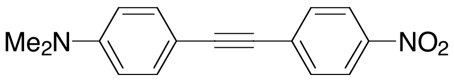
**For C**

http://www.lhup.edu/~rkleinma/Chem430/Practice/problems2.htm
At the above WWW page, you can see that 1,3,5,7-octatetraene has a main absorption at about 290 nm, again shorter than in C, apparently due to the rigidity of the structure of C.

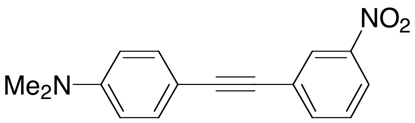
By Woodward analysis, this is a homoannular diene with two conjugation extenders, five alkyl substituents, and one OAc substituent, plus three exocyclic C=C. Predicted UV-vis max = 253 + (30 + 30) + (5*5 + 0) + (5 + 5 + 5) = 353 nm, slightly below the 356 nm observed, but pretty close, and clearly at much higher wavelength than the molecules with lesser conjugation.

In this problem, the trends are easily predicted by the linear nature of the chromophores, similarity of structures to one another, and the structural rigidity (no surprises due to conformational effects). But, the absolute numbers can be a challenge to predict, even with good empirical models.

(3) (10 pts) Structure P below shows a very strong UV-vis maximum peak shift going from nonpolar to polar solvents, while M shows a modest shift. Give a brief explanation for this different behavior.



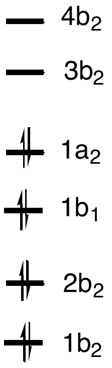
**P**



**M**

Since **P** is a through-conjugated system, there are good resonance and conjugation pathways between the electron acceptor –$NO_2$ and the electron donor –$NMe_2$. This allows for very strong polarization of some excited states in **P**, with the possibility for a large solvatochromic shift (presumably a red shift in this case, for a large $\pi-\pi*$ transition). The *meta*-connection in M destroys the possibility for direct through-conjugated interaction between the substituents, so one expects a smaller solvatochromic shift.

(4) (15 pts) for the hypothetical MO diagram shown below (molecule with $C_{2v}$ symmetry), work out the proper symmetry designation for the states formed by $2b_2$ to $3b_2$, $1b_1$ to $3b_2$, and $1a_2$ to $3b_2$ excitations. Which of these is/are symmetry allowed, and which symmetry forbidden? Show your work, using your group theory tables.



Well, dig out your $C_{2v}$ point group able, the same one used for examples in the lecture.

<u>For a $2b_2$ to $3b_2$ transition</u>, one gets a $(1b_2)^2\ (2b_2)^1\ (1b_1)^2\ (1a_2)^2\ (3b_2)^1\ (1b_2)^0$ electron occupancy diagram. Remember your simple guidelines for irreducible representations:

(a) $\Gamma_1 \times \Gamma_1 = \Gamma(\text{sym})$ [the totally symmetrical representation]
(b) $\Gamma_1 \times \Gamma(\text{sym}) = \Gamma_1$ [for any general irreducible representation]

The irreducible representation for the state formed by this transition is

$\Gamma = (b_2)^2(b_2)(b_1)^2(a_2)^2(b_2)$ (the product of reps of all orbitals times each orbital occupancy note that orbital reps take lower case, while states take upper case)

$\Gamma = (b_2)(b_2) = {}^1A_1$ (a singlet excited state, in the totally symmetric rep in $C_{2v}$)

The ground state for this molecule is also ${}^1A_1$, since it is closed shell (all orbitals are doubly occupied).

So, for the transition (${}^1A_1 \rightarrow {}^1A_1*$), we want $\Gamma_{\text{ground state}} \times \Gamma(\text{x,y, or z}) \times \Gamma_{\text{excited state}} = \Gamma(\text{sym})$. Simply look to see whether any of the Cartesian axes transforms as the product $\Gamma_{\text{ground state}} \times \Gamma_{\text{excited state}} = A_1 \times A_1 = A_1$

The z-axis transforms with $A_1$ in $C_{2v}$ , so the transition is symmetry allowed. This does not mean that it will be strong, but it is not required by symmetry to be weak or non-existent.

For a $1b_1$ to $3b_2$ transition, one gets a $(1b_2)^2$ $(2b_2)^2$ $(1b_1)^1$ $(1a_2)^2$ $(3b_2)^1$ $(1b_2)^0$ electron occupancy diagram.

The irreducible representation for the state formed by this transition is

$\Gamma = (b_2)^2(b_2)^2(b_1)(a_2)^2(b_2)$ (the product of reps of all orbitals times each orbital occupancy
note that orbital reps take lower case, while states take upper case)
$\Gamma = (b_1)(b_2) = {}^1A_2$ (a singlet state)

So, for the transition $({}^1A_1 \rightarrow {}^1A_2^*)$, we want $\Gamma_{\text{ground state}} \times \Gamma(x,y,\text{ or } z) \times \Gamma_{\text{excited state}} = \Gamma(\text{sym})$.
Simply look to see whether any of the Cartesian axes transforms as the product
$\Gamma_{\text{ground state}} \times \Gamma_{\text{excited state}} = A_1 \times A_2 = A_2$

No Cartesian axis transforms with $A_2$ in $C_{2v}$ , so the transition is symmetry forbidden. This requires by symmetry that the transition be weak to non-existent.

For a $1a_2$ to $3b_2$ transition, one gets a $(1b_2)^2$ $(2b_2)^2$ $(1b_1)^2$ $(1a_2)^1$ $(3b_2)^1$ $(1b_2)^0$ electron occupancy diagram.

The irreducible representation for the state formed by this transition is

$\Gamma = (b_2)^2(b_2)^2(b_1)^2(a_2)(b_2)$ (the product of reps of all orbitals times each orbital occupancy
note that orbital reps take lower case, while states take upper case)
$\Gamma = (a_2)(b_2) = {}^1B_1$ (another excited singlet state)

So, for the transition $({}^1A_1 \rightarrow {}^1B_1^*)$, we want $\Gamma_{\text{ground state}} \times \Gamma(x,y,\text{ or } z) \times \Gamma_{\text{excited state}} = \Gamma(\text{sym})$.
Simply look to see whether any of the Cartesian axes transforms as the product
$\Gamma_{\text{ground state}} \times \Gamma_{\text{excited state}} = A_1 \times B_1 = B_1$

The x-axis transforms with $B_1$ in $C_{2v}$ , so the transition is symmetry allowed. This does not mean that it will be strong, but it is not required by symmetry to be weak or non-existent.