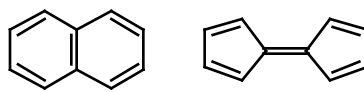


The Problems:

1. All alone one night in the lab, you pull a bottle of $C_{10}H_8$ off the shelf. It is oh-so-helpfully labeled “either naphthalene or difulvene” Unsatisfied with this uncertainty, you take an NMR spectrum and determine the ^{13}C chemical shifts to be 125.6, 127.7, and 133.3 ppm (relative to tetramethylsilane (TMS)). Note that the number and splitting pattern (not discussed here) of the peaks is *not* enough to distinguish between the hydrocarbon isomers.



naphthalene

difulvene

The network is down (no searching the Web) but your computer is working, so you decide to compute the NMR shifts for each possible compound and compare to your measurement. Since NMR calculations provide *absolute* isotropic chemical shifts, you will also need to do a calculation on TMS. To what point groups do TMS and each of the two hydrocarbons belong? *In order to complete this problem efficiently, you will absolutely need to ensure that you are providing the appropriate symmetry in your input geometries for all calculations!* Optimize all of the chemical structures at the HF/6-31G* level (as noted above, it may be more efficient to *start* with a smaller basis set, say STO-3G, to verify that you have the right symmetry and a decent starting geometry and force constants prior to doing the larger basis calculations). Now, compute the NMR shielding of ^{13}C in TMS at this level (the keyword required is simply **nmr**); what is the absolute isotropic shielding for this nucleus in ppm? Next, compute the isotropic shieldings of the unique ^{13}C nuclei in each of the two hydrocarbons at the same level (i.e., HF/6-31G* at the HF/6-31G* optimized geometries). Report these chemical shifts relative to TMS (which defines zero on the ppm scale for both nuclei). Which hydrocarbon is in the bottle? Explain why you consider your choice to be correct.

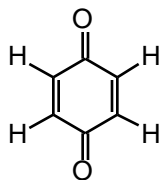
TMS belongs to the T_d point group, while both hydrocarbons belong to the D_{2h} point group. The very high symmetries of these point groups makes it possible to do reasonably good calculations with relatively little expended cpu time. The absolute shielding of the unique ^{13}C nucleus in TMS is 200.1 ppm at the HF/6-31G level. At the same level, the absolute shieldings for the 3 unique*

nuclei in naphthalene are 70.5, 75.7, and 78.0 ppm; the values for difulvene are 59.6, 69.7, and 81.5 ppm. If we now convert these to ppm relative to TMS we have 122.1, 124.4, and 129.6 ppm for naphthalene and 118.6, 130.4, and 140.5 ppm for difulvene. The former set of predicted data correlates perfectly with the measured values (I took them from the literature, by the way, I didn't make them up), although there is a systematic underestimation of about 3.6 ppm. The predicted data for difulvene, on the other hand, do not correlate very well at all.

Thermochemical data for difulvene are not available. However, experimental enthalpies of formation *are* available for benzene and fulvene (isomeric C₆H₆ analogs). What is the experimental difference in enthalpy between these two species at 298 K? What is the difference in energy between naphthalene and difulvene at the HF/6-31G* level (note: 1 E_h = 627.51 kcal/mol)? Is this consistent with the experimental difference for the smaller hydrocarbons? Why or why not? Compute the same energy difference for naphthalene and difulvene at the MP2/6-31G*//HF/6-31G* level. What do you conclude from comparing the HF difference to the MP2 difference?

The 298 K heats of formation for benzene and fulvene (NIST Webbook) are 82.9 and 224. kJ/mol, respectively. The computed difference in HF energies for naphthalene and difulvene is 257.1 kJ/mol. That is just slightly less than double the difference between benzene and fulvene, which is an intuitive result, especially since the resonance of naphthalene is less than twice benzene because of the fused nature of the ring system. At the MP2//HF level, the computed energy difference is 264.6 kJ/mol. This is a fairly small change as a function of adding correlation energy, which is pleasant, since it implies the correlation energies for the two systems are similar and we need consider the issue no further. (Or, of course, MP2 could be completely wrong, but we'll leave that for someone else to decide.)

2. Find the UV spectrum of quinone on the NIST website. There are 3 absorptions. Assuming each is well described as a single excitation (i.e., $a \rightarrow b$ where a is the occupied orbital from which the electron comes and b is the virtual orbital to which it goes) sketch a and b for each of the 3 absorptions.

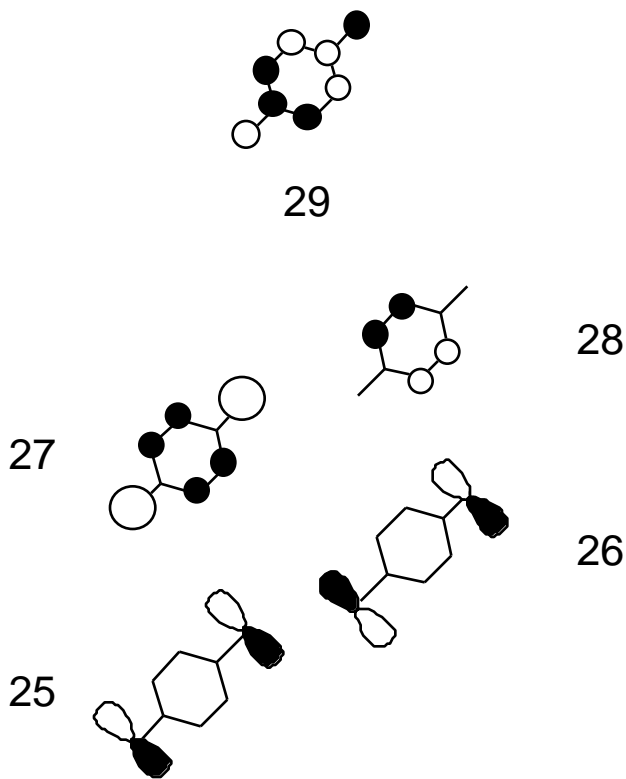


quinone

To do this, first optimize the structure of quinone at the RHF/6-31G* level (what point group should you take advantage of?). Then use the keyword line: `ci s(n=4) /6- 31G*`

`guess=read geom=checkpoint pop=regular` in a new input file. This will give you the excited state absorptions and oscillator strengths (using the cis formalism) and the MO coefficients. The CIS output includes a vector that describes the nature of each excited state in terms of contributions of different $a \rightarrow b$ possibilities. You need only worry about the largest contribution for each of these vectors. Instructions for how to generate a sketch of the MO's appears as an appendix to this problem set. Remember that CIS always *overestimates* the energy required to reach the excited state. You may also assume that the first two transitions overlap in the experimental spectrum and cannot be separately identified.

The first 4 absorptions occur at predicted wavelengths of 297, 279, 219, and 180 nm, respectively. The eigenvectors indicate the dominant excitations to be $26 \rightarrow 29$, $25 \rightarrow 29$, $28 \rightarrow 29$, and $27 \rightarrow 29$, respectively (i.e., every excitation populates the LUMO, but each from a different occupied orbital). Sketches of orbitals 25-29 are below.



Are the computed oscillator strengths consistent with the observed spectrum? Explain your answer.

Only the highest energy absorption is predicted to have a non-zero oscillator strength. As expected, it is a $\pi \rightarrow \pi^*$ process (although in very high symmetry there is no guarantee that this will be an allowed transition, as is indeed the case for the next lower energy transition). In the experimental spectrum, the extinction coefficient for the highest energy peak is on the order of

10^4 , consistent with an allowed transition. The others are weaker, consistent with “forbidden” transitions. NIST’s website does not specify whether the displayed spectrum is gas phase or not, unfortunately.

Finally, use Koopmans’ theorem to predict the ionization potential of quinone at the HF/6-31G* level. How does this compare with the experimental value?

The HOMO energy is 11.2 eV (after conversion from atomic units) compared to an experimental vertical IP of 10.1 eV. Not particularly good agreement in this case.

3. [No written analysis was required.]