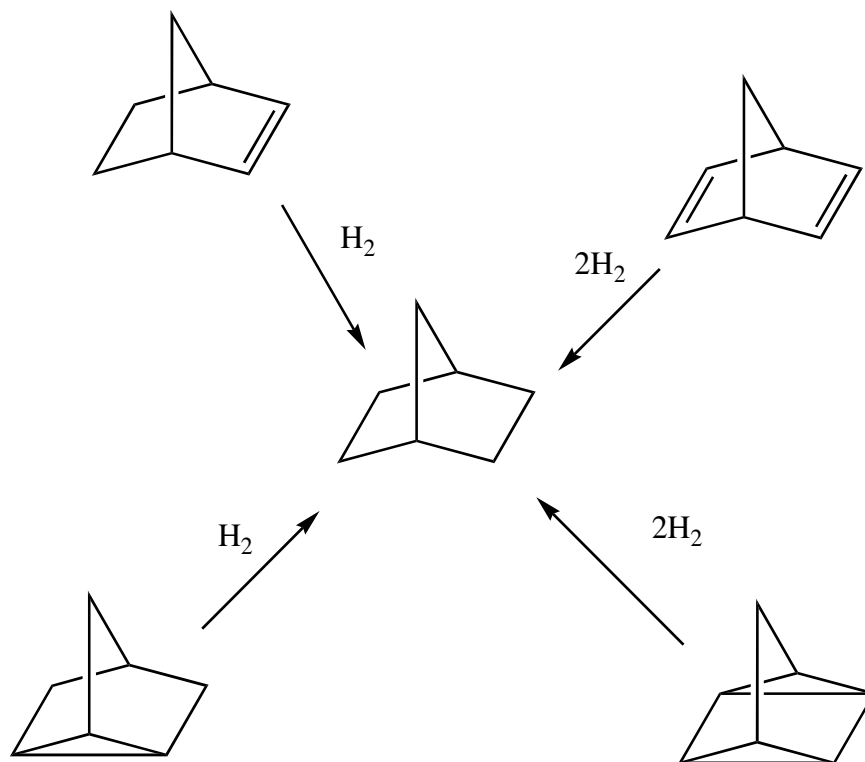1. For the organic molecules associated with norbornadiene below, fill in the table on the next page with predicted heats of formation.

Enthalpies of Formation (kcal/mol) of the Norbornadiene Cycle

Compound	MMX	AM1	PM3	Expt.
Norbornadiene	55.5	67.7	58.8	57.4
Norbornene	19.5	26.0	22.0	21.4
Norbornane	-12.8	-14.4	-13.7	-12.4
Nortricyclane	19.5	33.8	26.0	20.2
Quadricyclane	79.4	104.4	86.3	79.5

Comment on the data—are the models useful? Were they fast?

The molecular mechanics force field does a surprisingly good job at calculating the various heats of formation. One suspects that many of the subject molecules are in the training set, and/or that the atom types are fairly specific to the bicyclic systems. The semi-empirical methods have an accuracy ordering of roughly AM1 < MNDO < PM3 (somewhat unexpected since AM1 usually outperforms MNDO). The errors in the semiempirical methods are slightly higher than what one might like, but are not bad given their enormous speed.

Ensuring that you take advantage of symmetry (ask if you're in doubt about how to accomplish this—also, see Z-matrix handout on class website), compute the $\Delta H_{f,298}$ for quadricyclane (using its atomization energy and Table 10.2 in the text) at the HF/6-311G(2df,p), MP2/6-311G(2df,p)//HF/6-311G(2df,p), and TPSS/6-311G(2df,p)/auto levels (note that the keyword in Gaussian for TPSS is `tpsstpss`). Also compute $\Delta H_{f,298}$ using the G3 method (there is a G3 keyword in Gaussian 03). For the HF/6-311G(2df,p) level, demonstrate in detail how you did one of the calculations of the heat of formation.

	Quadricyclane
Method	ΔH_f(298K)
TPSS	72.8
HF	512.5
MP2	98.9
G3	81.6

For HF calculation:

$\Delta H_f(\text{predict},298K)$ quadricyclane $=$
$H(\text{HF},298K)$ quadricyclane
$-8H(\text{HF},298K)\,\text{H} - 7H(\text{HF},298K)\,\text{C}$
$+8\Delta H_f(\text{expt},298K)\,\text{H} + 7\Delta H_f(\text{expt},298K)\,\text{C}$

$$\Delta H_f \, (\text{predict}, 298K) \text{ quadricyclane in kcal/mol} =$$

$$627.5095 \times \begin{bmatrix} (-269.54922) - 8 \times (-0.49745) \\ -7 \times (-37.68732) \end{bmatrix}$$

$$+ 8 \times (52.103) + 7 \times (171.29)$$

Now, (symmetry again!) compute the 298 K enthalpy of norbornadiene *relative* to quadricyclane at the HF/6-311G(2df,p), MP2/6-311G(2df,p)//HF/6-311G(2df,p), TPSS/6-311G(2df,p)/auto, and G3 levels.

Answers are 23.1, 19.3, 16.7, and 23.6 kcal/mol where the experimental value is 22.1 kcal/mol.

Compare and contrast the various models with respect to speed and accuracy. What have you learned? If your research assignment were to learn how things would change if the methylene bridge in these systems were to be replaced with an oxygen atom, what level of theory would you use to do the calculations?

Considering the ab initio/DFT models, the absolute accuracy of HF is dismal, TPSS is better than MP2, but nowhere near as good as G3. The relative accuracy of HF is shockingly good -- nearly equal to G3. The other two models are not as good, and TPSS does surprisingly badly, because it does not show cancelling errors. So, if I was in a wicked hurry, I'd do the HF calculations to make my prediction. If I had lots of time, I'd then follow up with G3 to be sure. Of course, one could also hope the MM method would give a good result given its performance here.

Single level methods are known to do poorly in calculating heats of formation mostly due to their inability to adequately capture correlation energy. Molecules have vastly more correlation energy compared to their constituent atoms (since they have many more electrons than do each of the individual atoms), so if the model cannot accurately compute the correlation energy, this leads to large errors. Composite methods are designed to correct for incompleteness in the correlation energy and basis set size. They also sometimes have empirical terms to improve accuracy. As mentioned above, MM and SE models are parameterized for heats of formation, so their accuracy is founded on their training sets.

2.   In the attached communication from *Angewandte Chemie, International Edition in English*, Lambert et al. report the isolation and X-ray crystal structure of the
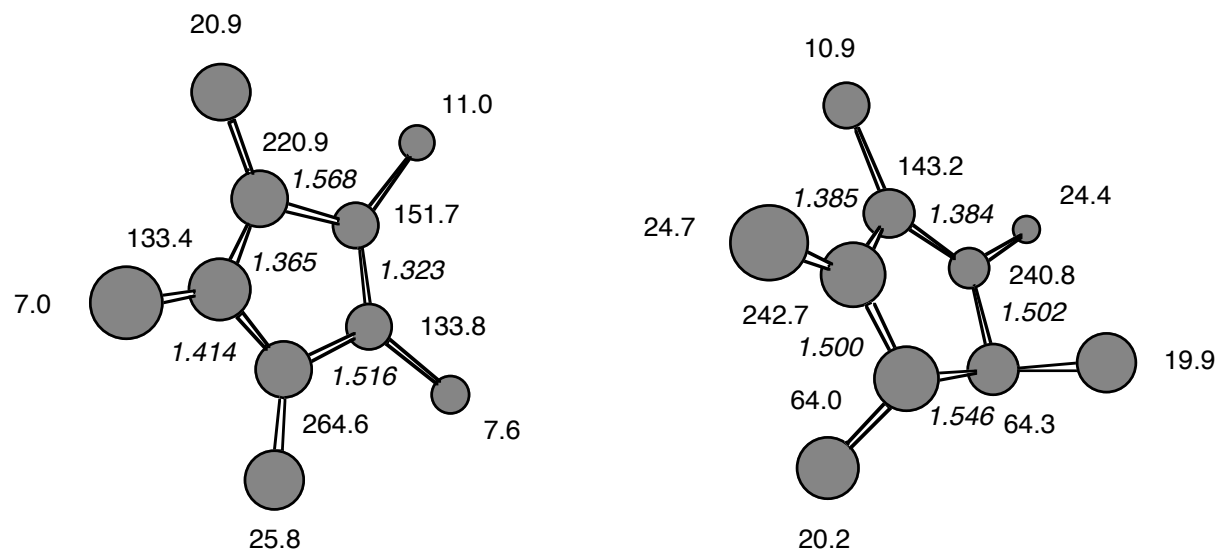
pentamethylcyclopentadienyl (Cp*) cation. Note that Cp*+ is formally antiaromatic, so its been an attractive synthetic target for many years.

Lambert et al. report structural data and ^{13}C NMR data. Optimize the structure of the Cp* cation at the HF/3-21G level (don't worry about trying to impose symmetry). How do your structural data compare to the reported data? Now compute the isotropic ^{13}C NMR chemical shifts for all carbons at the B3LYP/6-31G(d)//HF/3-21G level (simply include the keyword nmr in a single-point calculation). Since NMR calculations provide *absolute* shieldings, you will also need to know the computed shieldings for tetramethylsilane (TMS, which is the standard for δ = 0 on the ^{13}C chemical shift scale). I have done this calculation for you, and it may be found in the file ~cm8021pr/templates/tmsnmr.out (note the lovely T_d symmetry!). A *de*shielding ^{13}C shift δ is then determined as shielding for TMS minus shielding for carbon of interest. How do your data compare to those reported by Lambert et al.? (Use a picture to report your structural and NMR data).

Now consider the pentamethylcyclopent*eny*l cation (i.e., not *di*enyl, but just *mono*enyl; add the two H atoms trans to one another on adjacent carbon atoms). Compute structural and ^{13}C chemical shifts for this structure at the same levels of theory as already done for Cp*+. How do your data compare to those reported by Lambert et al.?

Which of these two molecules do you think was actually made?

Bond lengths and ^{13}C chemical shifts are noted in the below pictures (hydrogen atoms removed for clarity). Note that only in the mono-unsaturated ring does theory predict two methyl groups to be significantly out of the plane of the ring, as seen in the X-ray crystal structure. Agreement between theory and experiment is much better for the enyl system than for the dienyl system. To quantify this point, the RMS error in bond lengths for the most favorable overlap of the computed rings with the experimental one is 0.093 Å for the dienyl case and 0.022 Å for the monoenyl case. The RMS error in ring chemical shifts is 48 ppm for the dienyl case, and a mere 6.6 ppm for the monoenyl case.

20.9

11.0

220.9

1.568

151.7

133.4

1.365

1.323

7.0

1.414

133.8

1.516

264.6

7.6

25.8

10.9

143.2

1.385

1.384

24.4

24.7

242.7

240.8

1.502

1.500

64.0

19.9

1.546 64.3

20.2

So, what was really made? See Lambert and co-workers, *Angew. Chem., Int. Ed. Engl.* 41 (2002) 2275-2276 and 2278.

3.   Here begins a problem that will carry over to the third problem set and ultimately the final exam. Take a look at

    pollux.chem.umn.edu/8021/C5H8N2/

Full credit for sensible data.