

1. In class, we went through Hückel theory as applied to the allyl cation in considerable detail (following the textbook). Consider if the central C–H fragment in the allyl cation were to be replaced by the isoelectronic N: (with an in-plane lone pair). The 2-azaallyl cation is easily generated by deprotonation of *N*-methylformaldimine. Now, here are a few experimental facts: (i) the ionization potential of the methyl radical is 9.8 eV, (ii) the ionization potential of the amidogen radical is 10.8 eV, (iii) the rotational barrier of ethylene is 60 kcal/mol, (iv) the rotational barrier of formaldimine is 60 kcal/mol. Now, some questions: (i) what is the Hückel resonance energy for the 2-azaallyl cation? How do the 2-azaallyl system orbitals differ from the allyl system? Carry out AM1 calculations for the allyl and 2-azaallyl cations and visualize the orbitals; are they consistent with your predictions from Hückel theory? Compute the rotational barriers for a terminal methylene unit in allyl and 2-azaallyl; are they consistent with your predictions from Hückel theory?

Including an N atom in Hückel theory will require us to do several things. First, we must decide what basis function to put on the N; a $2p_z$ orbital seems obvious (just like for a C atom). Next, we need to define overlap matrix elements involving this orbital with others; using the same $\mathbf{S} = \mathbf{1}$ approximation as with all-C Hückel theory seems sensible. Finally, we need to know H_{ii} and H_{ij} for a N atom as atom i and a C atom as atom j (there's only one N atom in our system, so we don't need to worry about N–N interactions). By analogy to the all-C theory, we should make the H_{ii} value equal to the negative of the ionization potential (IP) of the corresponding mono-N species, which in this case is the amidogen radical, NH_2^\cdot . Since the $-\text{IP}$ of the methyl radical defines α , the data above suggest that we should use 1.1α for H_{ii} when i refers to an N atom. As for nearest neighbor interactions, since data suggest that the rotational barrier about $\text{H}_2\text{C}=\text{NH}$ is equal to that for $\text{H}_2\text{C}=\text{CH}_2$, we can evidently continue to use β for this quantity. In that case, the secular equation $|\mathbf{H} - E\mathbf{S}| = 0$ becomes

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & 1.1\alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (1)$$

Expanding this determinant using Cramer's rule gives

$$(1.1\alpha - E)(\alpha - E)^2 - 2\beta^2(\alpha - E) = 0 \quad (2)$$

One root for this equation is $E = \alpha$. Factoring this out from eq. 2, we have

$$(1.1\alpha - E)(\alpha - E) - 2\beta^2 = 0 \quad (3)$$

This is a quadratic in E , which may be more easily solved from expanding to

$$E^2 - 2.1\alpha E + (1.1\alpha^2 - 2\beta^2) = 0 \quad (4)$$

which has solutions

$$\begin{aligned} E &= \frac{2.1\alpha \pm \sqrt{4.41\alpha^2 - 4(1.1\alpha^2 - 2\beta^2)}}{2} \\ &= \frac{2.1\alpha \pm \sqrt{8\beta^2 + 0.01\alpha^2}}{2} \\ &\approx 1.05\alpha \pm \sqrt{2}\beta \end{aligned} \quad (5)$$

The final simplification is adequate for qualitative purposes (the term involving α in the square root changes the value of the square root by about 4%). If we really wanted quantitative accuracy, we could always plug back in the true energy values for α and β , but I'll focus here more on the qualitative aspects.

The first question was, what is the resonance energy of the 2-azaallyl cation? Putting two electrons into the lowest energy orbital would give a total energy of $2.1\alpha + 2\sqrt{2}\beta$. In the case where we rotate a CH_2^+ terminus out of conjugation, both electrons would go into the remaining $\text{H}_2\text{C}=\text{NR}$ double bond, which has energy $2.1\alpha + 2\beta$ (if that's not obvious, try doing the 2×2 secular equation, solve for the roots, and put 2 electrons in the lowest energy orbital). So, just as in the allyl cation system, the resonance energy is $(2\sqrt{2} - 2)\beta$, or about 0.86β (again, a very small amount *larger* in magnitude for 2-azaallyl if we hadn't ignored the 4% contribution from $0.01\alpha^2$ above).

Now, with those 3 value of E as roots for the secular equation, we can determine molecular orbital coefficients. Let's do the lowest-energy case first. The relevant system of linear equations is

$$\begin{aligned}
a_1[\alpha - (1.05\alpha + \sqrt{2}\beta) \cdot 1] + a_2[\beta - (1.05\alpha + \sqrt{2}\beta) \cdot 0] + a_3[0 - (1.05\alpha + \sqrt{2}\beta) \cdot 0] &= 0 \\
a_1[\beta - (1.05\alpha + \sqrt{2}\beta) \cdot 0] + a_2[1.1\alpha - (1.05\alpha + \sqrt{2}\beta) \cdot 1] + a_3[\beta - (1.05\alpha + \sqrt{2}\beta) \cdot 0] &= 0 \\
a_1[0 - (1.05\alpha + \sqrt{2}\beta) \cdot 0] + a_2[\beta - (1.05\alpha + \sqrt{2}\beta) \cdot 0] + a_3[\alpha - (1.05\alpha + \sqrt{2}\beta) \cdot 1] &= 0
\end{aligned} \tag{6}$$

Subtraction of the 3rd equation from the first establishes that $a_1 = a_3$. Making that substitution in the 2nd equation gives

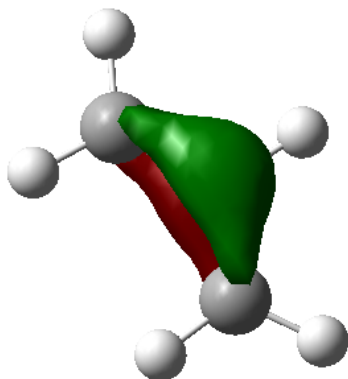
$$a_2[0.05\alpha - \sqrt{2}\beta] + 2\beta a_1 = 0 \Rightarrow a_2 = \left(\frac{2\beta}{\sqrt{2}\beta - 0.05\alpha} \right) a_1 \tag{7}$$

If we recall that both α and β are negative quantities, we see that the prefactor on the right-hand-side of eq. 7 is *greater* than $\sqrt{2}$ (plugging in numbers, the prefactor in eq. 7 is about 1.93 compared to $\sqrt{2}$ in the all-C allyl system, which is 1.41). Now, applying the normalization constraint

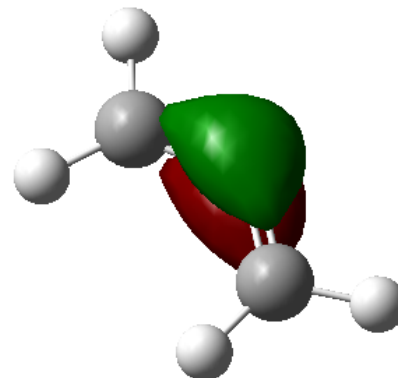
$$\begin{aligned}
\sum_{i=1}^3 a_i^2 = 1 &\Rightarrow a_1^2 + (1.93)^2 a_1^2 + a_1^2 = 1 \\
&\Rightarrow a_1 = 0.42, a_2 = 0.81, a_3 = 0.42
\end{aligned} \tag{8}$$

this can be compared to the case for all-C allyl, where the coefficients are 0.50, 0.70, and 0.50. Thus, the amplitude at the central N atom is *increased* in the lowest energy orbital. This result is as we would expect noting that the N is more electronegative than C (that's why its $-IP$ parameter is 10% larger than C).

Note that for the *second* orbital, the energy determined above ($E = \alpha$) does not differ from the allyl example that we did in class, and the solution of the linear equations is the same (coefficients of 0.70, 0.00, and -0.70). While the algebra is not shown here, solving for the highest energy MO will lead to a denominator in the prefactor analogous to that in eq. 7 that has "+" 0.05α , instead of minus. Thus, the coefficients end up as roughly 0.55, -0.62 , 0.55 (where for the all-C allyl case, they are 0.50, -0.70 , and 0.50); the contribution of N to this orbital is diminished (which is necessary, actually, to balance for its *enhanced* contribution to π_1). Looking at the orbitals in GaussView, one sees, for example:

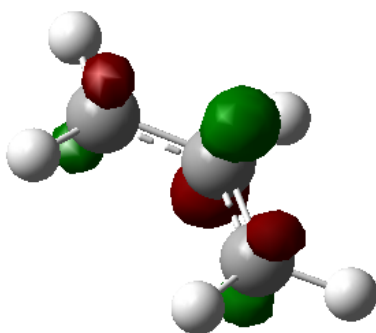


π_1 for all-C allyl system

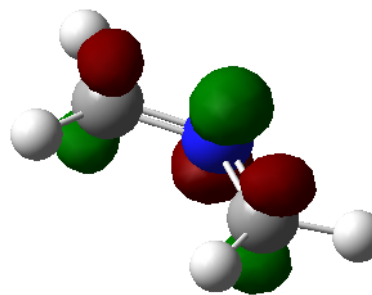


π_1 for 2-azaallyl system

where the greater contribution from the N atom to the 2-azaallyl system π_1 is clear (one does have to increase the isodensity value substantially to see this, since the bonding orbital is entirely in phase across all 3 atoms). One may see the variations in π_3 somewhat more readily because the orbitals are out of phase:



π_3 for all-C allyl system



π_3 for 2-azaallyl system

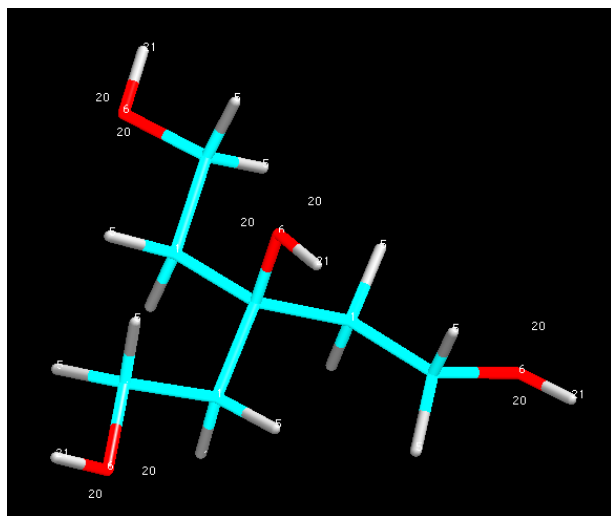
where now the greater contribution of the central atom relative to the outer atoms is indeed seen for the all-C allyl π_3 compared to the 2-azaallyl analog.

As for the rotational barriers, at the AM1 level, the rotational barrier for allyl cation is 18.6 kcal/mol. That's pretty close to what Hückel theory predicts (0.83β is 0.83×30 kcal/mol is about 25 kcal/mol). But, perhaps surprisingly, optimizing the rotated 2-azaallyl cation *lowers* the energy by more than 30 kcal/mol. The issue, of course, is that the result of rotation is a highly delocalized $\text{H}_2\text{C}=\text{N}=\text{CH}_2^+$ molecule that is conjugated in *both* directions (the two methylene groups are twisted 90° relative to one another) because N has p orbitals participating in both π systems (something a C atom can't do since it carries an H substituent). We

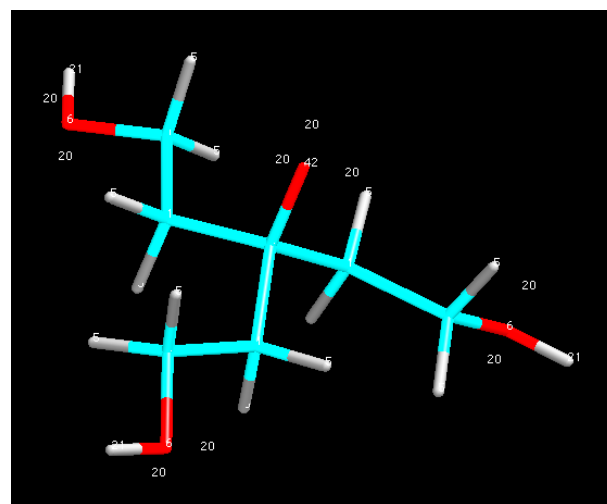
haven't discussed how to do Hückel theory with two *different* π systems, one in plane and one out of plane, so we'll just have to put this problem down, now.

2. In Problem Set 1, we computed the internal hydrogen bond energies for the Kass polyol and its conjugate base alkoxide form. Based on the differential "internal" solvation energies, we estimated the energetic effect of hydrogen bonding on the acidity of the Kass polyol (just the parent compound—you need not do the various methylated species) compared to *t*-butanol. For your best extended and internally hydrogen bonded structures from PC Model, repeat these calculations at the AM1, PM3, PM6, HF/6-31G(d), HF/6-31+G(d), and MP2/6-31+G(2df,p)//HF/6-31+G(d) levels and report your results. Comment on variations between the models and any interesting price/performance issues. For the HF/6-31G(d) level, compute frequencies and thermal contributions to free energy therefrom. By how much do these thermal contributions cause ΔG of internal hydrogen bonding to differ from ΔE ? How do the IR spectra of the extended conformers differ, qualitatively, from those of the internally hydrogen-bonded conformers?

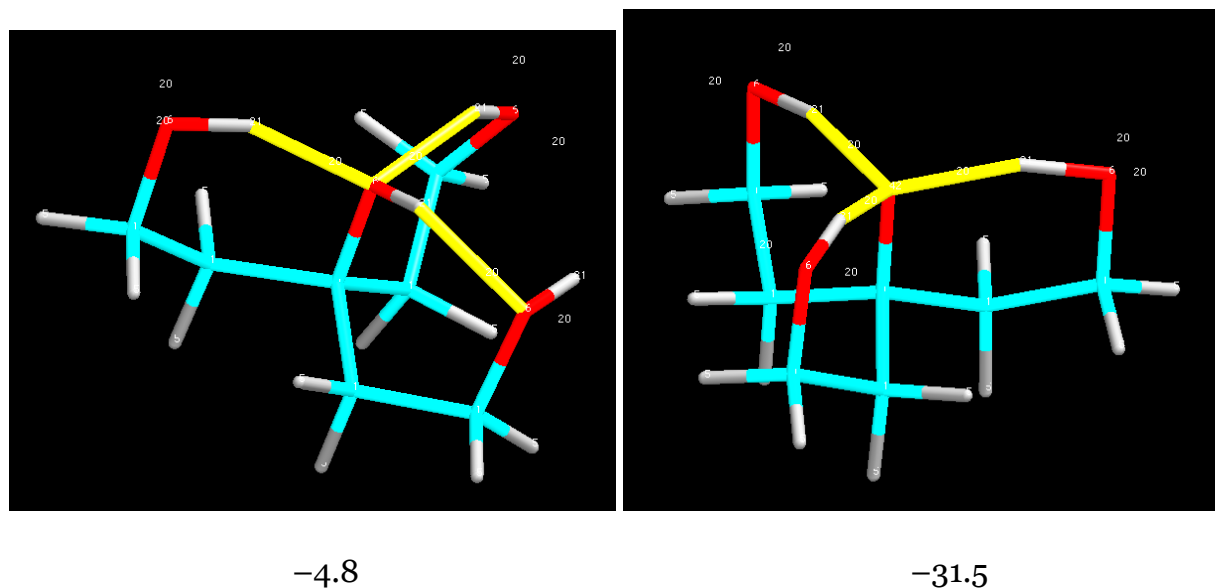
To remind us of the results from last round, with PC Model I found:



4.7



11.4



So, internal hydrogen bonding stabilizes the neutral minimum (relative to its fully extended conformation) by 9.5 kcal/mol, but the anion by 42.9 kcal/mol. Thus, the gas-phase acidity of the tetraol should be enhanced by about 33.4 kcal/mol compared to *t*-butanol (i.e., a final value of about 335 kcal/mol). That's roughly 24 p*K* units of enhanced acidity!

In the below table, I report the electronic energies from the requested levels of theory.

Computed Energies (E_h) of Polyols and Conjugate Bases

	Kass Polyol		Deprotonated Kass Polyol	
	Extended	Internal H-bonds	Extended	Internal H-bonds
AM1	-0.355 43	-0.365 29	-0.365 64	-0.386 33
PM3	-0.317 73	-0.327 72	-0.331 88	-0.373 80
PM6	-0.327 35	-0.335 63	-0.364 29	-0.393 61
HF/6-31G(d)	-573.788 10	-573.802 16	-573.181 57	-573.234 39
HF/6-31+G(d)	-573.809 59	-573.820 96	-573.216 12	-573.260 47
MP2/6-31+G(2df,p)// HF/6-31+G(d)	-575.943 15	-575.957 07	-575.363 93	-575.413 05

and these values lead to the following predictions for internal hydrogen bonding energies:

Computed Energies (kcal/mol) of Internal Hydrogen Bonding

	Neutral	Conj. Base
AM1	-6.2	-13.0
PM3	-6.3	-26.3
PM6	-5.2	-18.4
HF/6-31G(d)	-8.8	-33.1
HF/6-31+G(d)	-7.1	-27.8
MP2/6-31+G(2df,p)// HF/6-31+G(d)	-8.7	-30.8

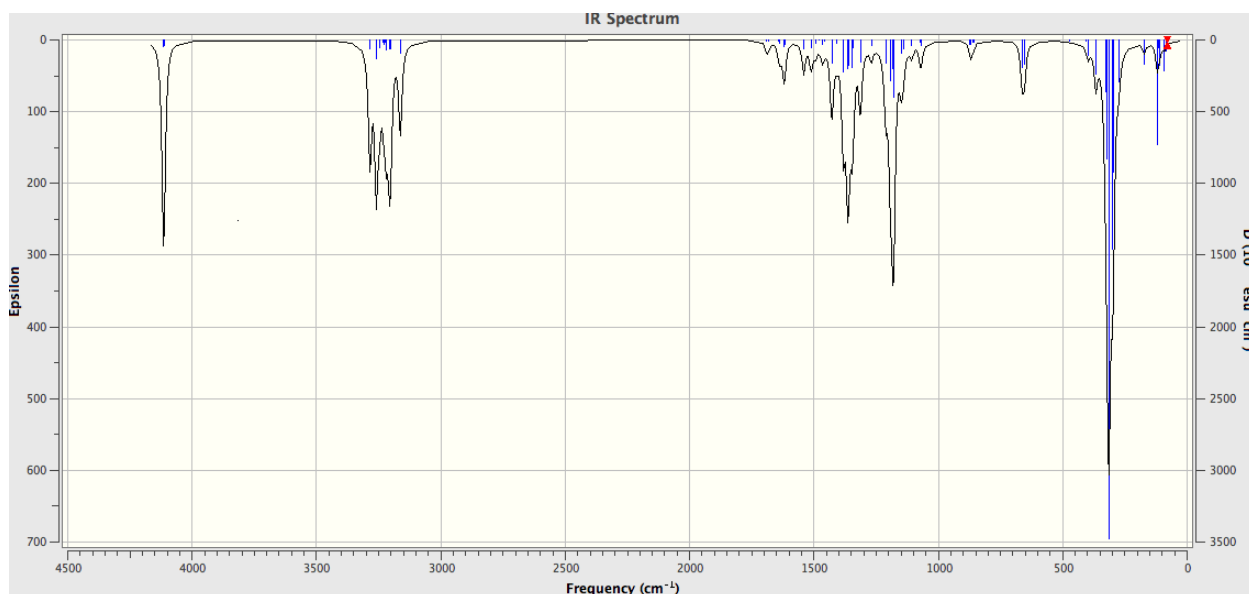
So, we certainly expect the best level to be MP2/6-31+G(2df,p)//HF/6-31+G(d). We see PC Model did OK for the neutral polyol (predicting 9.5 kcal/mol compared to this estimate of -8.7). For the anion, PC Model did much less well, overestimating the hydrogen bonding energy by 12.1 kcal/mol. All of the quantum models do OK for the neutral system, although PM6 is curiously worse than the older AM1 and PM3 models. For the anion, on the other hand, AM1 and PM6 are both very bad (poor hydrogen bonding was noted in AM1 from early on), but PM3 isn't bad. Indeed, PM3's differential hydrogen bonding prediction is 20 kcal/mol, while the best estimate is 22.1 kcal/mol (still a *lot* of pK units of acidity). None of these calculations were terribly time consuming, but PM3 was certainly more efficient than getting to MP2/6-31+G(2df,p)//HF/6-31+G(d), so getting to within 2 kcal/mol of correct is pretty good!

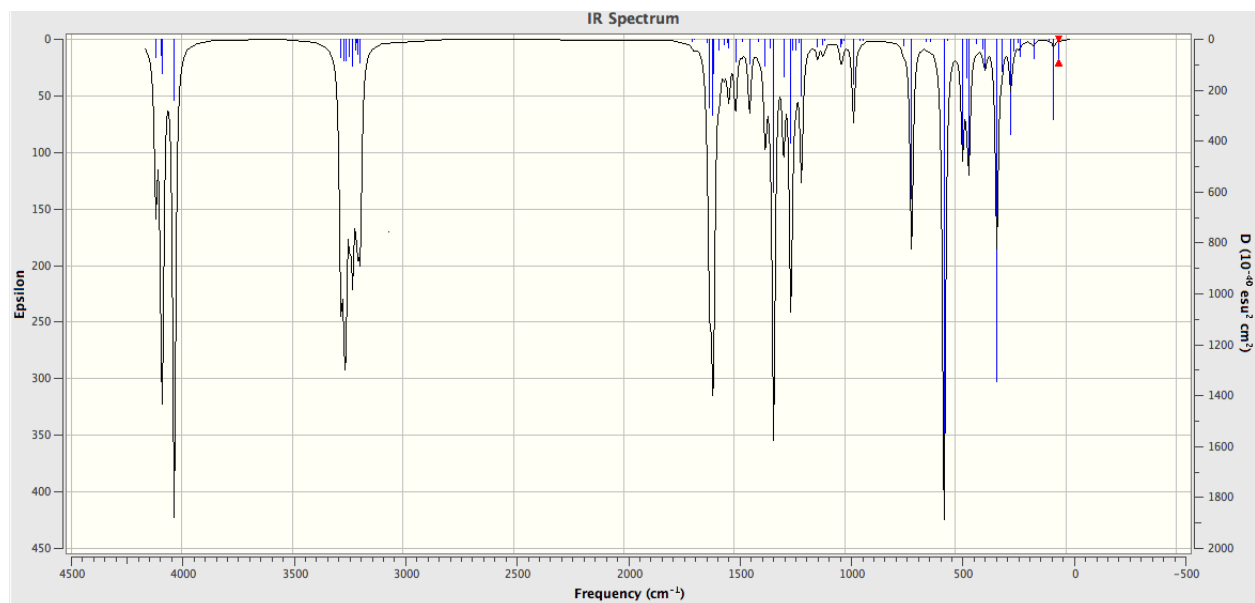
With respect to the ability of the levels of theory to make *absolute* predictions, I tested MP2/6-31+G(2df,p)//HF/6-31+G(d) (the best level that we're using here) for $t\text{-BuOH} \rightarrow t\text{-BuO}^- + \text{H}^+$, and computed $\Delta E = 381.2$ kcal/mol. As noted in the last problem set, the experimental deprotonation enthalpy is 368 kcal/mol. The difference between ΔE and ΔH favors products by about 10 kcal/mol (see below), so our best level underestimates the acidity of $t\text{-BuOH}$ by only about 3 kcal/mol. MP2 is actually a pretty good level for predicting acidities, but our basis set is still too small to fully stabilize the anion (that's why we're *underestimating* the acidity). Of course, we could use this error to correct our estimates for the Kass polyol if we wanted to have more quantitative estimates without doing more calculations.

The frequency calculations permit us to compare energies, enthalpies, and free energies for internal hydrogen bonding and deprotonation. Thus, at the HF/6-31G(d) level, the internal hydrogen bonding is favored for the neutral with ΔE , ΔH , and ΔG values of -8.8, -7.9, and -6.5 kcal/mol, respectively. The reduction in free energy compared to potential energy derives from the

“tightness” of the internally hydrogen bonded structure (less entropy) compared to the extended structure. Similarly, for the conjugate base form, the corresponding values are -33.1 , -31.7 , and -27.4 . Thus, the much larger “tightness” in the anion leads to a larger loss of free energy upon forming internal hydrogen bonds. Net effect is to reduce differential favoring the anion from 24.3 to 20.9 kcal/mol: still a big acidity enhancement, but lowered 3.4 kcal/mol from loss of entropy.

The last part of the question deals with the IR spectra (available from the frequency calculations) that permit differentiation of extended conformers from internally hydrogen bonded ones. As shown below, where the spectrum for the extended conformation is shown before that for the internally hydrogen bonded one

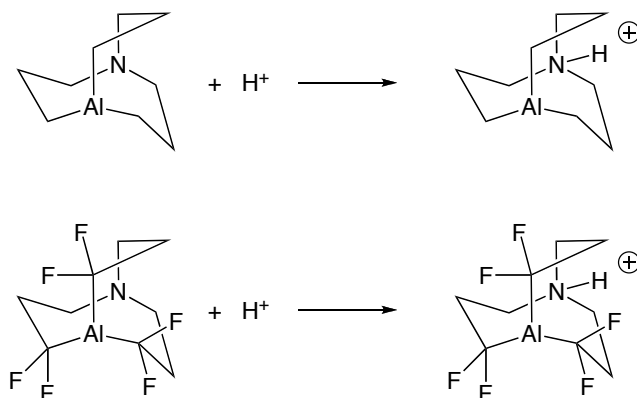




We can see that there is more richness in the OH stretching region for the internally hydrogen-bonded conformer (and also in the fingerprint region).

While not shown in this answer key, the comparison for the anions has the dramatic difference that the extended conformation has all OH stretches sharp above 4000 cm^{-1} but the internally hydrogen-bonded stretches are red-shifted to about 3500 cm^{-1} and broadened.

3. Consider the bicyclic alazane molecules on the next page, and in particular their basicities. Compute, at the levels indicated in the below tables, Al–N bond lengths optimized at the indicated levels of theory (consider: are there possibilities for bond-stretch isomerism?) and proton affinities at the indicated levels of theory. In some detail, discuss your modeling strategy and results, addressing in particular the chemistry, but also considering how the semiempirical models compare to the more complete levels of wave function theory. *Nota bene:* sensible attention to job ordering and symmetry will help you to stay within the development queue time limits as you work on this problem. Imagine that this problem was motivated by a question from an experimental colleague, namely, “How does the basicity of the alazane compare to that of the hexafluoroalazane?”



Taking advantage of the C_3 symmetry of these species makes this problem tractable. Failing to do so leads to painfully slow optimizations at, say, the MP2 level. A practical approach, if one does not want to try to *generate* a C_3 geometry by hand, is to do an initial optimization at a semiempirical level, note the “near” C_3 character of the optimized geometry, and then take advantage of GaussView’s ability to complete the “symmetrization” of such structures.

Al–N Bond Lengths (Å) in Alazanes

	Bicyclo[3.3.3]alazane		Hexafluorobicyclo[3.3.3]alazane	
	Unprotonated	Protonated	Unprotonated	Protonated
AM1	1.850	3.113	1.833	3.183
PM3	1.879	2.511	1.885	2.520
PM6	1.996	3.102	2.027	3.205
HF/3-21G	2.013	3.247	2.002	3.373
HF/6-31G(d)	2.065	3.256	2.061	3.363
MP2/6-31G(d)	2.061	3.255	2.065	3.390

Computed Energies (E_h) of Alazanes

	Bicyclo[3.3.3]alazane		Hexafluorobicyclo[3.3.3]alazane	
	Unprotonated	Protonated	Unprotonated	Protonated
AM1	-0.065 28	0.211 33	-0.502 07	-0.178 11
PM3	-0.062 37	0.252 05	-0.519 55	-0.186 28
PM6	-0.080 01	0.172 98	-0.630 31	-0.337 50
HF/3-21G	-644.152 20	-644.460 25	-1234.110 89	-1234.374 31
HF/6-31G(d)	-647.665 11	-647.984 50	-1240.793 06	-1241.074 68
MP2/6-31G(d)// HF/6-31G(d)	-649.067 55	-649.376 33	-1243.198 66	-1243.473 04
MP2/6-31G(d)	-649.069 39	-649.378 70	-1243.204 64	-1243.479 72

Note that the semiempirical levels compute heats of formation, *not* electronic energies, so the proton affinities are computed as the protonated heat of formation, minus the neutral heat of formation, *minus the heat of formation of a bare proton* (an experimentally known quantity, 367.2 kcal/mol—but not computable in *G09* as there are no electrons...) Of course, the same balanced chemical equation applies to the ab initio levels, but there the energies are electronic energies (not heats of formation) and the electronic energy of a bare proton is defined to be zero. In any case, the proton affinities are:

Computed Proton Affinities of Alazanes (kcal/mol)

	Proton Affinity		
	Alazane	Fluoroalazane	Fluoro effect
AM1	-193.6	-163.9	29.7
PM3	-169.9	-158.1	11.8
PM6	-208.5	-183.5	25.0
HF/3-21G	-193.3	-165.3	28.0
HF/6-31G(d)	-200.4	-176.7	23.7
MP2/6-31G(d)// HF/6-31G(d)	-193.8	-172.2	21.6
MP2/6-31G(d)	-194.1	-172.6	21.5

If we assume that the MP2 level (boldface black) is the “best” in terms of accuracy, we can color code other results: boldface green if within 1 kcal/mol of MP2, and normal blue if within 5 kcal/mol of MP2. AM1 is quite good for alazane, but less good for the fluoro case, so that it does quite poorly in predicting the effect of fluorination on acidity. PM3 is very bad, period. PM6 is improved compared to PM3, and its protonation error is systematic so that the fluorination effect is predicted within 3.5 kcal/mol (about 2.5 pK units at room temperature; not bad), which certainly beats the other semiempirical levels. Given that Al was probably a very exotic atom at the time AM1 and PM3 were developed (compared to PM6), this is not too surprising a result.

The HF/3-21G level accidentally does very well for alazane, but much less well for fluoroalazane. Inclusion of d functions in the basis set causes HF/6-31G(d) to make more systematically accurate predictions, although absolute proton affinities are overestimated by 4-6 kcal/mol. The MP2//HF predictions are *very* good for both the absolute proton affinities *and* the fluorination effect. Given the much, much higher cost of the MP2 optimizations, the single point MP2//HF model is clearly an outstanding choice from an energetic standpoint.

As for geometries, the semiempirical AM1 and PM3 models predict the Al–N dative bonds in the unprotonated species to be quite a bit too short, PM6 and HF/3-21G are better (but still too short), and HF/6-31G(d) is quite accurate. PM3 is a complete disaster for the Al–N distances in the protonated cases (weird), AM1 and PM6 predict distances too short by about 0.1 Å (that’s quite a lot), and the remaining models are all quite similar. The good agreement between the HF/6-31G(d) and MP2/6-31G(d) geometries rationalizes the high quality of the MP2//HF single-point predictions.

Note that AM1 predicts “open” bicyclo geometries that lack an Al–N dative bond in the unprotonated species. They’re a few kcal/mol higher than the internally bonded geometries. This appears to be an artifact for this semiempirical model, as no other level appears to predict such geometries (generated by simply deleting the proton on the open protonated geometries) to be stationary for the neutral species.

4. 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/PES/

Full credit for this problem is awarded for sensible data.