

1. Get a copy of Armstrong, A.; Chivers, T.; Parvez, M.; Boéré, R. T. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 502.
- a. Construct a Z-matrix for compound **2a** in that article, but with all THF ligands removed and all methyl groups replaced by H atoms. Write the Z-matrix in such a way that the structure has C_3 symmetry (your Z-matrix may be in either Gaussian or AMSOL format) and in such a way that the various bond lengths reported in Figure 1 of the *Angewandte* article agree with your Z-matrix structure to within 0.2 Å. E-mail your Z-matrix to Casey as clear text when you are satisfied that you have successfully completed this portion of the problem (so that he can verify it has the proper symmetry and meets the geometry constraints).

The below Z-matrix has the appropriate C_3 symmetry. Making the bond lengths work out is simply a trial and error exercise of varying the parameter values that converges rather quickly.

```

0 2
X
Br 1 5.
x 2 r1 1 90.
Li 3 r2 2 90. 1 180.
Li 3 r2 2 90. 1 60.
Li 3 r2 2 90. 1 -60.
X 2 r3 1 90. 3 0.
N 7 r4 2 90. 1 0.
N 7 r4 2 90. 1 120.
N 7 r4 2 90. 1 -120.
P 2 r5 1 90. 3 0.
N 2 r6 1 90. 3 0.
Si 2 r7 1 90. 3 0.
H 13 r8 2 ba 8 d1
H 13 r8 2 ba 9 d1
H 13 r8 2 ba 10 d1
C 8 r9 11 bb 2 180.
C 9 r9 11 bb 2 180.
C 10 r9 11 bb 2 180.
H 17 r10 8 bc 11 d2
H 17 r11 8 bd 11 d3
H 17 r12 8 be 11 d4

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H	18	r10	9	bc	11	d2
H	18	r11	9	bd	11	d3
H	18	r12	9	be	11	d4
H	19	r10	10	bc	11	d2
H	19	r11	10	bd	11	d3
H	19	r12	10	be	11	d4

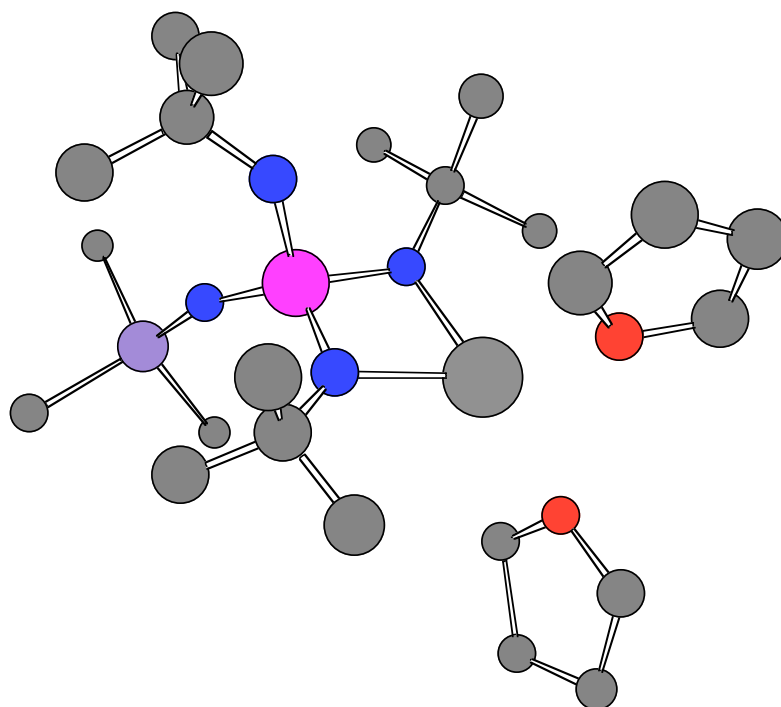
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r1=1.0
r2=1.5
r3=2.0
r4=1.5
r5=2.8
r6=4.3
r7=6.0
r8=1.4
ba=110.
d1=10.
r9=1.45
bb=125.
r10=1.1
r11=1.1
r12=1.1
bc=110.
bd=110.
be=110.
d2=50.
d3=170.
d4=-70.

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b. Optimize structure **3'** at the MNDO level of theory including two tetrahydrofuran ligands on the Li atom (see Scheme 1 and in-text drawing). Note that **3'** is a radical anion, so use the keywords UHF and CHARGE=-1 in your calculation. Once you are satisfied that you have a reasonable structure (you are welcome to ask Casey or me for our opinion on that front) compute ESR hyperfine coupling constants to compare to those reported on p. 503 of the article for this putative structure in solution. Carry out this calculation for your MNDO-optimized structure but at the B3LYP level using the MIDI! basis set for all atoms but Li and using the 3-21G basis set for Li (a template file is provided to show how to set up this mixed-basis set calculation).

Below is my MNDO structure with H atoms removed for clarity. Because of the tetracoordinate phosphorus it would be much better to use MNDO/d, which I originally did on my Macintosh using Chem-3D, but then discovered that the Wintel machines in the computer lab were limited to MNDO (go figure...) The structure changed, but not enormously



c. Are your computed splittings consistent with the experimental data (keep in mind that solution experiments measure the absolute value of an isotropic hyperfine coupling constant and thus *cannot distinguish* negative and positive values)? If your results are not perfectly consistent with experiment, thoughtfully discuss what other computational approaches you might take in order, in principle, to improve agreement with experiment (if you think that possible—if you think the structure is just totally wrong, you may attempt to support that position, too). In that discussion, address any practical issues that might arise in doing any calculations you suggest.

A single point calculation of the ESR hyperfine couplings provided (only heavy atoms shown):

Atom	a.u.	MegaHertz	Gauss	$10(-4)$ cm ⁻¹
1 N(14)	0.03580	11.56826	4.12784	3.85876
2 P(31)	-0.03891	-70.47514	-25.14728	-23.50798
3 N(14)	0.01692	5.46693	1.95074	1.82357
4 N(14)	0.08556	27.64537	9.86455	9.22150
5 N(14)	0.00154	0.49637	0.17712	0.16557
6 C(13)	-0.00561	-6.30325	-2.24916	-2.10254
7 C(13)	-0.00238	-2.67085	-0.95302	-0.89090

8	Si(29)	-0.00239	-2.12528	-0.75835	-0.70892
9	C(13)	-0.01478	-16.61533	-5.92876	-5.54228
10	C(13)	0.00530	5.95328	2.12428	1.98580
11	C(13)	0.00229	2.57082	0.91733	0.85753
12	C(13)	0.00297	3.34353	1.19305	1.11528
13	C(13)	0.00534	6.00173	2.14157	2.00196
14	C(13)	0.00045	0.50079	0.17870	0.16705
15	C(13)	0.00116	1.30100	0.46423	0.43397
16	C(13)	-0.00010	-0.11078	-0.03953	-0.03695
17	C(13)	0.00083	0.92961	0.33171	0.31008
18	C(13)	0.00063	0.70309	0.25088	0.23453
19	C(13)	0.00524	5.88688	2.10059	1.96365
20	C(13)	0.01048	11.77920	4.20311	3.92912
21	C(13)	0.03583	40.28510	14.37472	13.43766
58	Li(7)	-0.00109	-1.89424	-0.67591	-0.63185
59	O(17)	-0.00048	0.28997	0.10347	0.09673
60	C(13)	-0.00067	-0.75813	-0.27052	-0.25289
61	C(13)	-0.00002	-0.02177	-0.00777	-0.00726
62	C(13)	-0.00000	-0.00056	-0.00020	-0.00019
63	C(13)	-0.00005	-0.05782	-0.02063	-0.01929
72	O(17)	-0.00033	0.19821	0.07073	0.06611
73	C(13)	-0.00052	-0.58409	-0.20842	-0.19483
74	C(13)	-0.00002	-0.02537	-0.00905	-0.00846
75	C(13)	-0.00003	-0.03598	-0.01284	-0.01200
76	C(13)	-0.00003	-0.03366	-0.01201	-0.01123

The mean unsigned error in magnitude for predicted vs. experimental hyperfine couplings (the ones in red above) was about 1.9 G—decent performance, if not stellar (particularly not stellar in that the MNDO structure does NOT predict the two nitrogens with hfs values of 5.38 G to be equivalent). Note that the ^{13}C hfs values do not complicate the spectrum because the natural abundance of ^{13}C is only 1% (same story for ^{29}Si), while the magnetically active ^7Li , ^{14}N , and ^{31}P nuclei are the dominant contributors to natural abundance for these elements.

2. Get a copy of Saraf, S. R.; Rogers, W. J.; Mannan, M. S.; Hall, M. B.; Thomson, L. M. *J. Phys. Chem. A*, **2003**, *107*, 1077.

a. Verify the reported G2, G2MP2, G3, G3B3, and CBS-Q numbers reported in Table 3 for rxns 1 and 2. Show how you carry out at least one such verification of a number in the table and report enthalpies for all necessary species.

I'll just do one example, the G3B3 level. The 298 K G3B3 enthalpies of hydrogen, ammonia, water, hydrogen peroxide, and hydroxylamine are (au) -1.16417, -56.50448, -76.37994, -151.46368, and -131.62891 respectively. Experimental heats of formation (298 K, kcal/mol) for the first four are 0.0 (by definition), -10.98, -57.80, and -32.58, respectively. For equation (1), heat of formation of hydroxylamine is computed as

$$0.0 - (-57.80) - (-10.98) + \{ 627.5095 * [(-76.37994) + (-56.50448) - (-1.16417) - (-151.46368)] \} = -11.46 \text{ kcal/mol}$$

(Note the conversion factor 627.5095 kcal mol⁻¹ au⁻¹ appearing in the braces) The sense of the equation is that heat of formation of unknown reactant is equal to computed heat of reaction plus experimental heat of formation of known reactants minus experimental heat of formation of products.

That value is in acceptable agreement with the reported value of -11.51 (the 0.05 kcal/mol difference is probably attributable to the geometry difference in hydroxylamine from optimization criteria not being screwed down to extra-tight values).

b. Compute the 298 K enthalpy of formation for hydroxylamine using its atomization energy at the 5 indicated levels and the table at the end of this problem set (which corrects errors in Table 10.2 of the textbook). Again, show the equations/values you used to accomplish this calculation.

The computed G3B3 enthalpies for H, N, and O are -0.49873, -54.56280, and -75.02993. An approach identical to that used above is employed, except that the reaction is hydroxylamine → 3H + N + O, there are no known reactants (only the unknown) and the experimental atomic heats come from the table at the end of the problem set. I compute a heat of formation for hydroxylamine of -10.03 kcal/mol by this protocol.

c. How do your answers from part a compare to those from part b? If there is a difference, which number(s) do you trust more? Explain your reasoning.

In the example that I've done, the two values differ by a fairly substantial 1.5 kcal/mol. Isodesmic equations are always more trustworthy than raw atomization calculations (provided that the errors on the known components are low...)

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/C4H6N2O2-PES/

When prompted, your username is chem## (your SP account ID) and your password is that part of your e-mail address preceding "@umn.edu". If you have any problems, see Casey.

While there, select **View Surface**. You will see my contribution to mapping the C₄H₆N₂O₂ surface (click on [chem01.html](#) to see it in 3D -- if working from home, you will need to get the Chime Plug-in if you don't already have it -- if you don't have the plug in, or can't seem to get it to work, you'll see text cartesian coordinates, which you can always visualize in Chem-3D after pasting them into a text file, adding a new first line with the total number of atoms (14), and opening it as cartesian coordinates from Chem-3D). My point on the surface is a transition-state structure for the retro-Diels-Alder cycloreversion of 3,6-dihydroxy-3,6-dihydropyrazine to make *s-cis E,E*-1,4-dihydroxy-1,3-butadiene and molecular nitrogen.

Your task is to find a point of your own on the potential energy surface (PES)—either a minimum or a transition state—*that is not already in the table* (easy if you're the first to finish, harder and harder the longer you wait...) To complete an entry, you will need a frequency calculation at the HF/6-31G(d) level (and thus, of course, you will first have to have optimized the structure at this level of theory). When you have the data, click on **Submission Form** and paste in the number of imaginary frequencies (0 or 1), the HF energy, enthalpy, and free energy, and finally the optimized cartesian coordinates (you can cut and paste right from the output file of the frequency calculation). If you make any mistakes, you can delete an entry and start again.

Full credit for any unique minimum or TS structure having the correct formula.