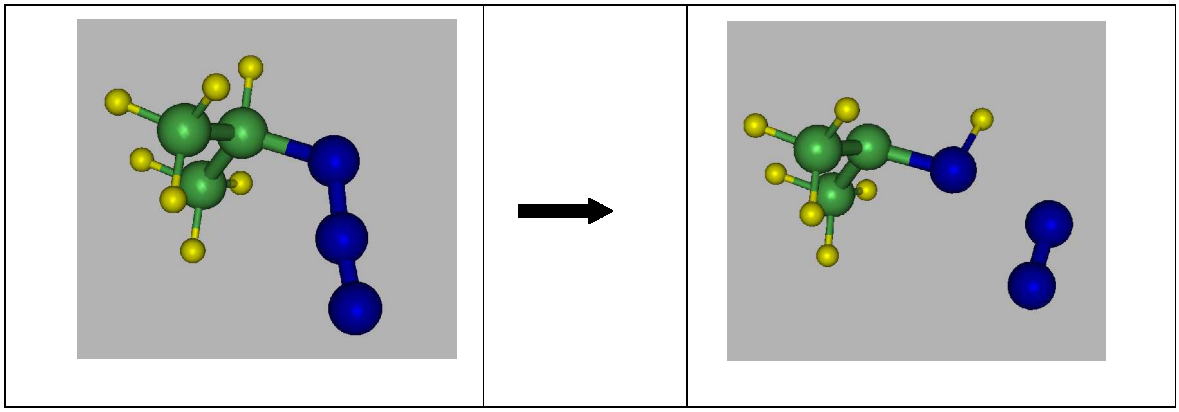
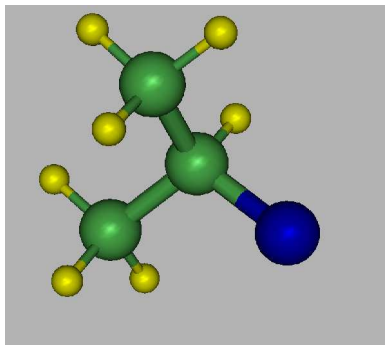
Modeling an Elimination/Migration Reaction:

Overview of this Exercise

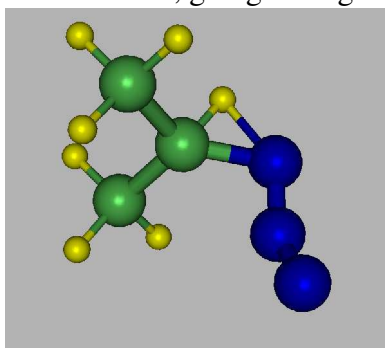
We are interested in studying the mechanism for the process of N_2 elimination and hydrogen migration in isopropylazide:



The question is whether the reaction occurs via a nitrene intermediate:



or if the elimination and migration are concerted, going through a transition structure such as:



Finally, we would like to know how the answer to this question is influenced by the nature of the migrating group. For instance, what would happen if the hydrogen were replaced by a methyl group?

The reaction is exothermic at all levels of theory considered. However, the B3LYP/6-31G(D) model predicts the process to be concerted while the HF/STO-3G and HF/6-31G(D) models predict that a nitrene intermediate is formed. The true nature of the mechanism is still being debated in the literature. See references :

Experiments:

Linke, Tissue, Lwowski, JACS **89**, 6308 (1967).

H. Bock and R. Dammel, JACS **110**, 5261(1988).

G. Bertrand, J.D. Majoral, A. Baceirdo, Acc. Chem. Res. **19**, 17 (1986).

M.S. O'Dell, B. DeB. Darwent, Can. J. Chem. **48**, 1140(1970).

See also J. March, "Advanced Organic Chemistry," 3rd edition, Wiley and Sons, New York, page 984.

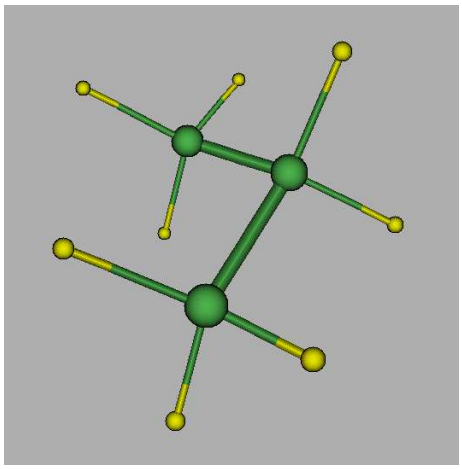
CASSCF Calculations showing nitrene intermediate for methyl azide decompostion:

J.F. Arenas, J.I. Marcos, J.C. Otero, A. Sanchez-Galvez, J. Chem. Phys. **111**, 551 (1999).

Detailed Instructions

Building of the Molecule

1. If Gabedit is not already running, go to a unix command window and type the command "gabedit".
2. Click on Draw/Display Geometry icon.
3. On Area zone click with right button of mouse and select Add/Attach functionals group/Isopropyl (please note that molecule is available by 1.1.5 version of gabedit), and click to Area zone.



Experiment with the mouse at this point :

* Select the “Rotate” icon (right of window)
  - see the note at the bottom of window.
  - Move the mouse while holding down the left button to rotate.
  - Move the mouse while holding down the midle button to rotate.
* Select the “Zoom” icon (right of window) :
  - See the note at the bottom of window.
  - Move the mouse(top-bottom or bottom-top) while holding down the left button

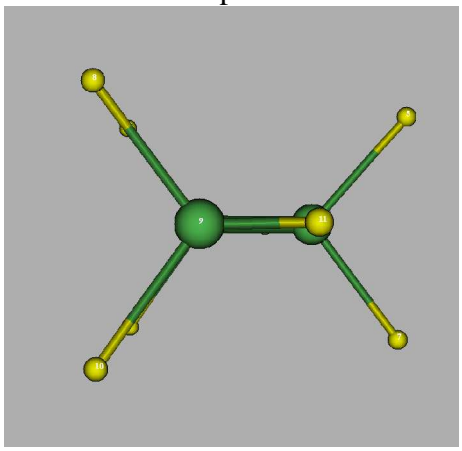
to zoom.
- Move the mouse while holding down the midle button to rotate.

* Select the “Translate” icon (right of window) :
  - See the note at the bottom of window.
  - Move the mouse while holding down the left button to translate.
  - Move the mouse while holding down the midle button to rotate.

* Select the “Mesure” icon (right of window) :
  - click with right button of mouse and select Labels/Numbers
  - click with right button of mouse and select Labels/Distances

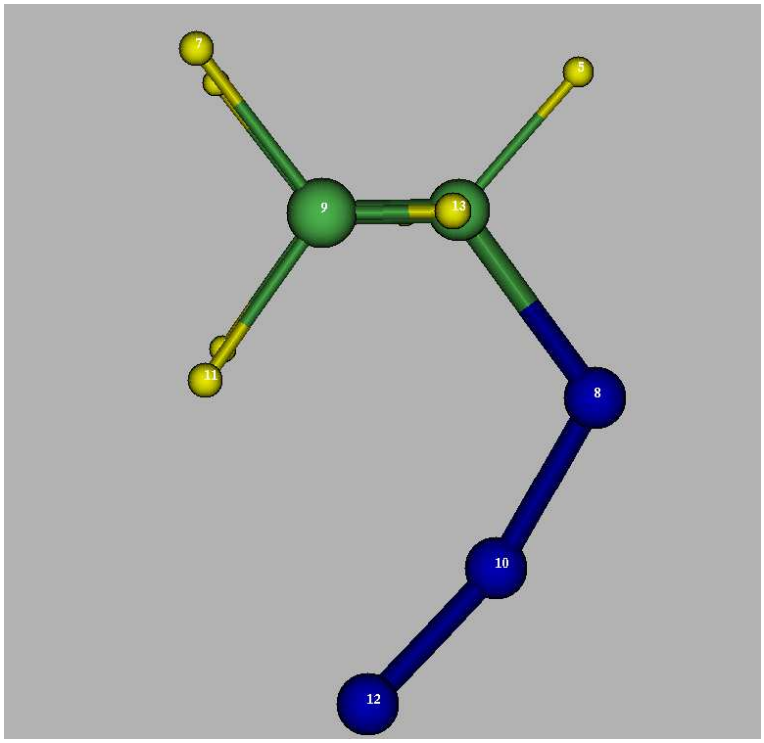
* Select the “Mesure” icon (right of window) :
  - See the note at the bottom of window.
  - Select one, two, three or four atom. The distance , angle and dihedral angle are display to the left notebook of window.
  - Move the mouse while holding down the midle button to rotate.

4. Select the “Insert a atom” (pencil). Click on the H button and select Nitrogen when the periodic table appears.
   Move the mouse while holding down the midle button to rotate to obtain the hydrogen atoms bonded to the central carbon in the plane of the window.



   Now Click (left button of mouse) on one hydrogen atom connected to the central carbon. The hydrogen atom is replaced by N atom (N_1).
5. Select the “Move selected atoms”. Click on the N atom and move the atom to obtain a distance = (approximately) 1.4 Ang between N_1 and C.
6. Select the “Insert a atom” (pencil).
   Now Click (left button of mouse) (not on a atom of molecule) to add a second N atom(N_2).
   Select the “Move selected atoms”. Click on the N_2 atom and move the atom to obtain a distance = (approximately) 1.2 Ang between the N_2 and N_1 atoms.
7. Select the “Insert a atom” (pencil).
   Now Click (left button of mouse) (not on a atom of molecule) to add a third N atom(N_3).
   Select the “Move selected atoms”. Click on the N_3 atom and move the atom to obtain a distance = (approximately) 1.1 Ang between the N_3 and N_2 atoms.

You have successfully built the desired structure :



Optimizing the Molecule

1. Close Geometry Windows. Choose File/New Gaussian input (or Gaussian icon) from the principal Menu.
2. Select Hartree Fock at Method Frame.
3. Select STO-3G at Basis Frame.
4. Select Geometry Optimization at Type Frame.
5. Click to NEXT button.
6. Click to FINISH button.
7. Using gabedit text editor for replace Opt(Redundant,MaxCycle=20) by fopt=CalcAll
8. Click to Run molpro/Gaussian icon (toolbar, top of window).
9. At save data file in text zone , type azid_HF_STO3G
10. Click to OK button.
11. Gaussian is now started at background job.
12. Select azid_HF_STO3G.log notebook.
13. Click to Update/End for reload the output file of Gaussian.
14. When the job completes (and this may take several minutes) : click to Geom. Conv. Button(right of window) for discover various optimized values for this structure. In particular, write down in your notebook the values of the H-N bond distance (the migrating proton), the H-C-N bond angle, as well as the two N-N bond distances. You may wish to record other geometric features as well. View the Gaussian logfile to obtain information about the Enthalpy and Free energy (you can search using Search icon).
    Select the last point and click to Draw button.

Transition state for N_2 Elimination

1. Starting with your optimized isopropylazide structure, change the N_1-N_2 bond length 1.7 : For this :
    - Move the mouse while holding down the midle button to rotate to obtain the hydrogen

atoms bonded to the central carbon in the plane of the window.
- Select “Selection of atoms” icon, click to window (left button) and move your mouse for select N_2 and N_3 atoms.
- Select “Movie selected atoms” icon, click to a selected(N_2 for example) atom and move your mouse to obtain a distance = 1.7 between N_1 and N_2 atoms.

2. Close Geometry Windows. Choose File/New Gaussian input (or Gaussian icon) from the principal Menu.
3. Select Hartree Fock at Method Frame.
4. Select STO-3G at Basis Frame.
5. Select Geometry Optimization at Type Frame.
6. Click to NEXT button.
7. Click to FINISH button.
8. Using gabedit text editor for replace Opt(Redundant,MaxCycle=20) by opt=(calcall,ts,noeigentest)
9. Click to Run molpro/Gaussian icon (toolbar, top of window).
10. At save data file in text zone , type azid_HF_STO3G_TS
11. Click to OK button.
12. When the job completes, once again note the important bond distances and angles for the structure. Record these as well as the energy in your notebook. The difference between this energy and the one recorded for azide structure is the barrier energy for this process. You should compute this and convert it to kcal/mole. You can also look at the Gaussian logfile to obtain information about the Enthalpy and Free Energy.
13. At this point we should investigate what transition structure we have found.
    Click to “Display Density/Orbitals/Vibration” icon(toolbar, top of window).

    Click to “Close” button for close the window with contains the list of orbitals.
    Click with right button and select “Vibration” from menu. A new window is displayed.

    At the new window, with rigth button of mouse, select “Read Gaussian output file” and select azid_HF_STO3G_TS.log file.
    The negative frequency vibration corresponds to the motion through the saddle point on the potential energy surface. Click "Start" to animate this vibration. How should you describe this motion? Which mechanism have we found for this transition state?

    You can modify the scale parameter (type “Enter” after modification).

Increase Basis Set Size

Now return to each of your structures and submit a new gaussian job for each where you have changed the basis set to 6-31G(d). Use different file names - do not destroy the data from the runs completed so far). This basis set includes polarization functions on the carbons and nitrogens and includes both an outer and inner sp shell on each as well. These calculations will take much longer to complete. Summarize your results in terms of geometries and energies.

Use Density Functional Theory

Return once again to your structures and submit new gaussian jobs which use the 6-31G(d) basis set but also the B3LYP theoretical model. How do the results now compare?

Methyl group Migration

Now repeat the entire study using t-butylazide. We are now investigating the migration of the methyl group. Use only the B3LYP/6-31G(d) model this time and compare to the results you obtained from the proton migration study.