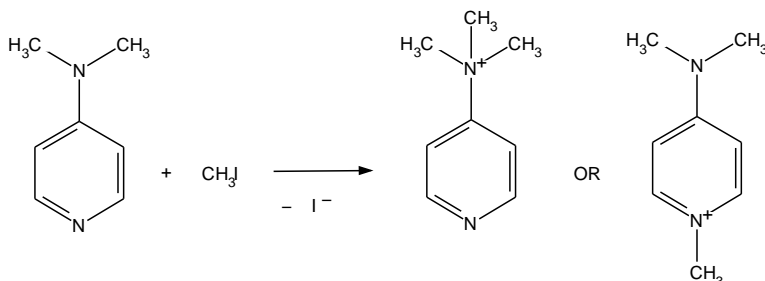


Table 1: Calculated Energies of DMAP and derivatives

	AM1	RHF/6-31G*
DMAP	-139,619 kJ/mole	-379.77999206 a.u.
4-( <i>N,N</i> -dimethylamino)-1-methylpyridine	-155,356 kJ/mole	
4-(trimethylamino)pyridine	-155,241 kJ/mole	
DMAP + CH <sub>3</sub> I: Near pyridine N	-189,496 kJ/mole $r_{N-CH_3} = 3.39$	
DMAP + CH <sub>3</sub> I: Near dimethyl amine N	-189,495 kJ/mole $r_{N-CH_3} = 4.17$	

## 4-(*N,N*-dimethylamino)pyridine - DMAP

DMAP is a common organic base. Last period, we reacted this molecule with CH<sub>3</sub>I to produce a methylated cation. Based on NMR analysis, the structure of this product could be determined. We will now examine results of theoretical calculations compare with our experimental results.



## Energy Calculations

In computational chemistry, the energy of molecules and ions can be calculated. For isomeric compounds, the more negative energy corresponds to the most stable structure. Results from AM1 (a fast, but approximate method) and RHF/6-31G\* (a more rigorous, but much slower method) calculations are presented below. Results from these calculations are shown in Table 1.

AM1 calculations were also performed to show the interaction of DMAP with CH<sub>3</sub>I. In these calculations, the methyl iodide was aligned in preparation for the S<sub>N</sub>2 reaction. The energy differences for attack by the pyridine ring N-atom and the amino N-atom were small, but the N...C distances were very different. These differences can be used to infer something about the reactivity of the two different types of N atoms.

## Electrostatic Potential Energy Surfaces

In addition, maps of the electrostatic potential for DMAP were also calculated. In these maps, the attraction/repulsion felt by a hypothetical charge at points around a molecule are calculated, resulting in a 3-dimensional map showing strongly electrophilic and nucleophilic locations. The maps resulting from the AM1 calculations were very similar to those resulting from the RHF/6-31G\* calculations, and are shown in

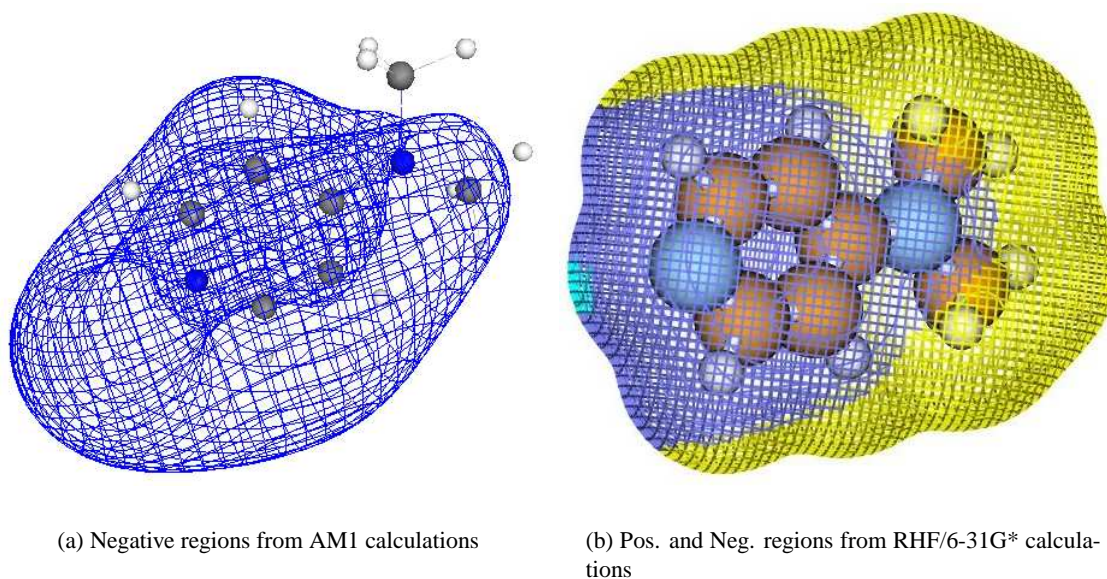


Figure 1: Calculated Electrostatic Potential Maps of DMAP

Figure 1. For the RHF/6-31G\* map, both the positive and negative surfaces are shown in different colors, while for the AM1 map, only the negative surface is shown since this is the surface that is relevant for the reaction we examined for this molecule.

### Laboratory Report

Your laboratory report will not include the standard sections included in all of your other reports. (No Introduction or experimental section). For the experimental results, you need to include the balanced equation, yield, %yield, and m.p. for the product obtained and a detailed analysis of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra provided in your laboratory book.

For the theoretical analysis, discuss (i) what the calculated energies suggest for the relative stabilities of the two different products, (ii) what the calculated energies and bond lengths suggest about the interaction of DMAP with  $\text{CH}_3\text{I}$ , and (iii) what the ESP surface suggests about reactivity of DMAP.