2.4: Exercise Questions

1. Consider the structure of N,N-dimethylacetamide show below. Using your knowledge of resonance please draw the two additional resonance structures associated with this compound. For full credit, please show the curved arrows used to interconvert these structures.

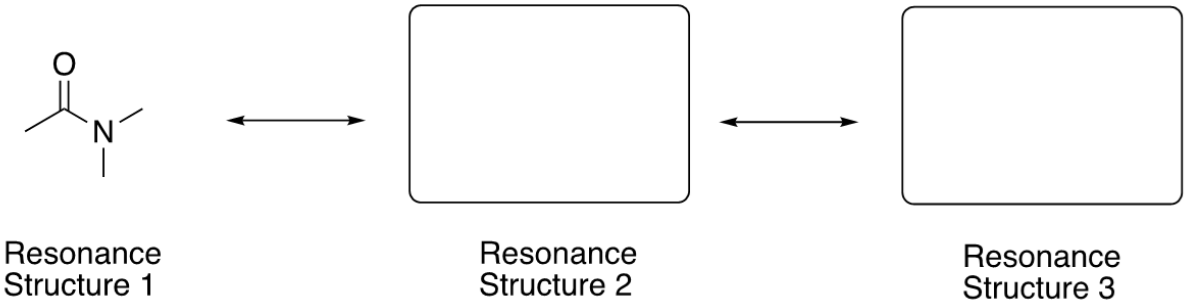

Figure 2.4.1: Copy and Paste Caption here. (Copyright; author via source)

2. Please average the structure of the three resonance structures and draw a resonance hybrid representing a more realistic picture of the electronic structure of the molecule (using dashed lines to indicate partial bonds).
3. In Avogadro, open the DMA.xyz file produced by ORCA and measure values indicated in the structure below.

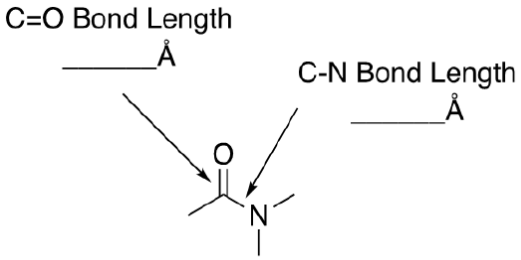

Figure 2.4.1: Copy and Paste Caption here. (Copyright; author via source)

4. To find computational evidence of electron delocalization we need to compare the bond length values of DMA to similar bonds that don't have the ability to form resonance structures with the lone pair on nitrogen. To do this we will examine bond lengths on acetone and trimethyl amine.
   A. Open the geometry coordinate files for acetone and dimethylamine in Avogadro and measure the values indicated in the structures below so that we can compare them to the bond lengths in DMA.

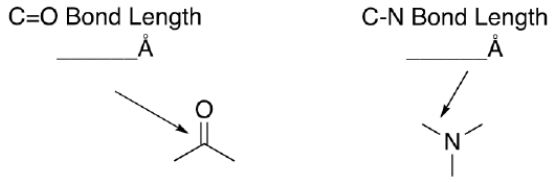

Figure 2.4.1: Copy and Paste Caption here. (Copyright; author via source)

   B. Calculate the % difference in bond lengths between the $C=O$ bond in acetone and that in DMA.

$$\%\ \text{Difference} = \frac{(\text{Bond Length DMA-Bond Length Acetone})}{\text{Bond Length Acetone}} \times 100\%$$

   C. Calculate the % difference in bond lengths between the C-N bond in trimethylamine and that in DMA.

$$\%\ \text{Difference} = \frac{(\text{Bond Length DMA-Bond Length Trimethylamine})}{\text{Bond Length Trimethylamine}} \times 100\%$$

   D. Given the % difference calculations what do you think the bond order (single, double, 1.5 etc.) is for the $C=O$ and $C-N$ bonds in DMA? Please make a prediction for both the $C=O$ and $C-N$ bonds. Does this fit with the resonance hybrid that you constructed above? Please explain.

5. One of the ways in which resonance works is that electrons communicate between bonds and atoms via a network of unhybridized P orbitals. For example, in methyl vinyl ketone each of the atoms involved in the resonance associated with the molecule has an unhybridized p-orbital

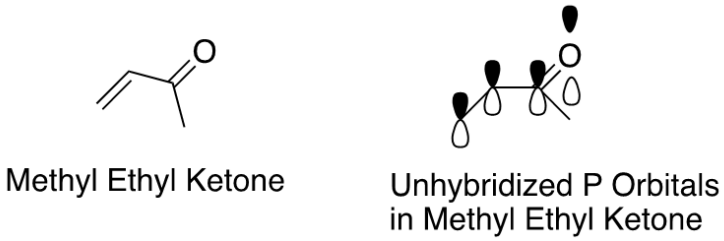

Figure 2.4.1: Copy and Paste Caption here. (Copyright; author via source)

A. Using your knowledge of VSEPR and hybrid orbital theory please indicate what the electronic geometry, molecular geometry, and hybridization would be expected to be of the nitrogen atom.

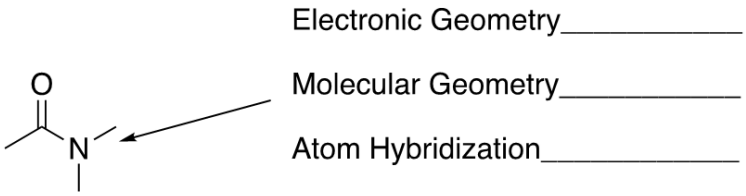

Figure 2.4.1: Copy and Paste Caption here. (Copyright; author via source)

B. Examine the dimethylacetamide output file and determine the molecular geometry of the nitrogen atom. What geometry best describes its bonding.

C. Using your answer from B. What hybridization best fits the geometry you described above? Does it have an unhybridized P orbital that the nitrogen could use to delocalize electrons via resonance?
