



Following the reaction path of the $\text{CH}_3\text{CN} \leftrightarrow \text{CH}_3\text{NC}$ isomerization

Bởi:

Thanh Truong

Reaction mechanism is a central concept in chemistry. This experiment shows you how to use molecular modeling tools to investigate reaction mechanism using the $\text{CH}_3\text{CN} \leftrightarrow \text{CH}_3\text{NC}$ reaction as an example.

There are three important steps in this procedure:

1. Determining structures of the reactants, products, and transition state.
2. Verify the transition state is the correct one, i.e. it connects the reactants and products.
3. Confirm the mechanism by following the reaction path from the reactants to products.

Procedure: Using tools in Avisto. You can download Avisto from Astonis.

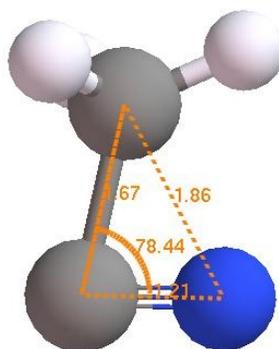
Step 1: Determine geometries of reactants, products, and transition state

This step involves generate good initial guesses for the structures of these species.

- Use MolDesign to create 3D structures for CH_3CN and CH_3NC . The 3D structures for these two molecules generated by MolDesign are already good guesses. For the transition state, it is more challenging since you need to use some chemical intuition to guess the 3D structure of the transition state for a given reaction. For this reaction, the methyl group migrates from the C atom to the N atom. One can guess that the transition state would have the methyl group in the middle of the C and N atoms such as in the figure below. In addition the reaction involves breaking the C-C bond and forming the C-N bond. Thus, at the transition state, the CC bond should be elongated (usually

Following the reaction path of the $\text{CH}_3\text{CN} \leftrightarrow \text{CH}_3\text{NC}$ isomerization

by 20-30%) and the CN bond is also formed (usually by 20-30% longer than the equilibrium value).



- Use Basic Qchem Edu or Basic QChem to search for the stable structures for CH_3CN reactant and CH_3NC product and to search for the transition state from the guess structure above.

Step 2: Verify the transition state is correct, i.e. the one corresponds to the migration of the methyl group from the carbon atom to nitrogen atom.

- Use the structure of the transition state results from Step 1, perform the vibrational analysis using the same Basic QChem Edu or Basic QChem tool. Note that you should check to make sure that the final structure from Step 1 should be at a stationary point as indicated in the last line of the Configuration Properties tab prior to perform the vibrational analysis. Vibrational frequencies are meaningful only when the configuration is at a stationary point.
- When open the results of the vibrational analysis with PsiViewer, the first vibrational mode should be a negative value. To be rigorous this frequency should be an imaginary number, however, for simplicity in printing the text file, it is often printed as a negative number. Select this mode then right-click to select 'Show vibration' to animate to vibrational mode. The motion should correspond to the motion of the methyl group moving between the C and N atoms.

At this point, it is often sufficient to conclude that the transition state structure that you found is the correct. You can calculate the reaction energy by the difference between the heats of formation of the product and reactant and the classical barrier height is the difference between the heats of formation of the transition state and the reactant.

Step 3: For large and complex reaction, to confirm the above results, you should also perform a reaction path calculation.

Following the reaction path of the $\text{CH}_3\text{CN} \leftrightarrow \text{CH}_3\text{NC}$ isomerization

- Use the results for the transition state in Step 1 as input for the reaction path calculation using the same tool.
- When viewing the reaction path results, in the potential curve tab, right click to select 'Start animation' to see how the structure changes as the reaction proceeds from the reactant to the product. Note that you can select C and N atoms then edit the bond type for a number of configurations to get the correct bond type when going through the animation.

