D1CH9116 - MMCO

Molecular Modelling applied to organic chemistry

Practical 3: Potential energy surfaces

A/ 1D Potental Energy Surfaces

1/ Use the *Reaction Path* tool of AGUI to visualize the evolution of the total energy (heat of formation) of the CH_3-CH_2-CH_2–CH_3 molecule as a function of the torsional angle. Evaluate the magnitude of the rotational barrier and compare to experimental data.

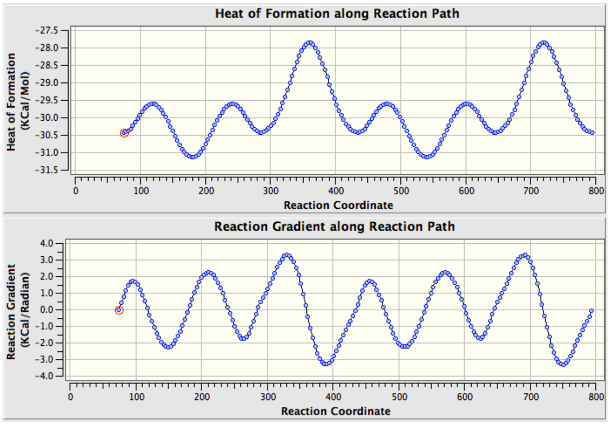


Figure 1. Evolution of the heat of formation (top) and gradient (bottom) with respect to the dihedral angle in the CH_3-CH_2-CH_2–CH_3 molecule.

The energy curve exhibits minima, which correspond to the stable structures (anti and gauche) of the butane molecule, as well as maxima, which correspond to transition structures connecting minima. The rotational barriers evaluated at the AM1 level are reported in the Table below together with experimental data.

rotational barrier / kcal.mol^{-1}	**AM1**	**Exp.**
From anti to gauche	0.7	0.8
From anti to anti	4-6	3.3

2/ Visualize the evolution of the total energy as a function and the formation of the co-ordinate (dative covalent) bond between ammonia and boron trifluoride:

$$NH_3 + BH_3 \rightarrow H_3N{-}BH_3$$

The *Reaction Path* tool of AGUI should be used here by specifying the B-N distance as the reaction coordinate.

Other examples of co-ordinate bond formations:

Reaction between ammonia and hydrogen chloride: $NH_3 + HCl \rightarrow NH_4Cl$

Dissolving hydrogen chloride in water to make hydrochloric acid: $H_2O + HCl \rightarrow H_3O^+ + Cl^-$

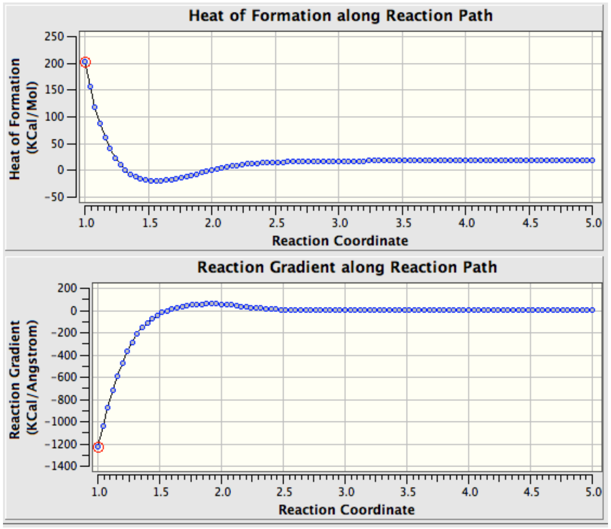


Figure 2. Evolution of the heat of formation (top) and gradient (bottom) with respect to the N-B distance along the formation of the co-ordinate bond between ammonia and boron trifluoride.

The energy curve exhibits a minimum, which correspond to the equilibrium structure of the $H_3N–BH_3$ molecule. The equilibrium B–N distance is equal to 1.56 Å. Note the change in the geometry of the BH_3 fragment, which becomes planar as the distance increases (going from an sp^3 to an sp^2 hybridization). On the contrary, the NH_3 fragment remains pyramidal due to the lone pair of the nitrogen.

3/ Energy profile of the hydroxycarbene–formaldehyde conversion.

a. Visualize the evolution of the total energy along the hydrogen migration in the intramolecular hydroxycarbene–formaldehyde conversion. The *Reaction Path* tool of AGUI should be used here by specifying the ONH angle as the reaction coordinate.

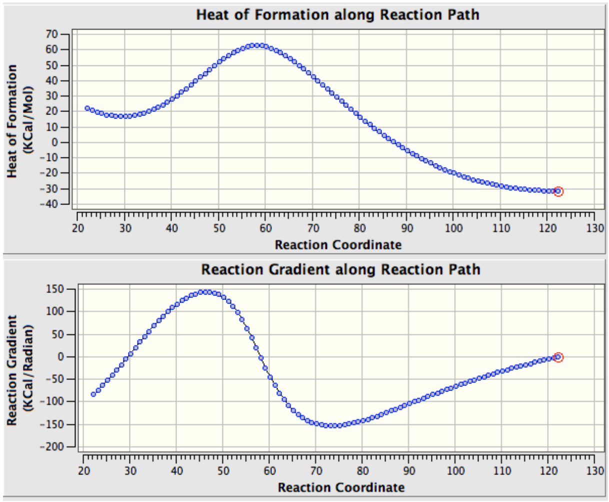


Figure 3. Evolution of the heat of formation (top) and gradient (bottom) with respect to the ONH angle along the hydrogen migration in the hydroxycarbene–formaldehyde conversion.

The energy curve exhibits a maximum connecting the two minima associated to the stable HCN and HNC isomers. In the transition structure, one of the H atoms lies in between the carbon and nitrogen atoms. The barrier is about 46 kcal/mol at the AM1 level.

b. Copy/paste the geometry of the transition structure in a new window, and compute the vibrational frequencies (*job=opt+freq with gradient minimization*). Confirm that the structure corresponds to a first-order saddle point of the PES, by checking the presence of a single imaginary wavenumber arising from a negative force constant. Use the graphical interface to check that this vibrational mode actually corresponds to the reactive process under study.

The transition-state structure is characterized by a negative force constant equal to -2.01702 millidynes/Angstroms, giving rise to a single imaginary wavenumber with a norm of 2617 cm^{-1}. The TS structure is illustrated on the figure below, along with the atomic displacement vectors associated to the imaginary frequency.

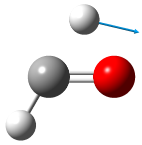
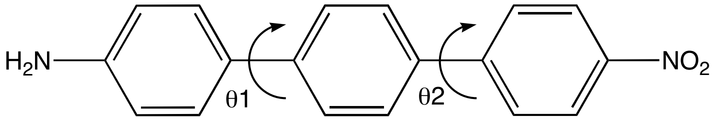


Figure 4: TS structure and atomic displacement vectors associated to the imaginary frequency.

B/ 2D Potential Energy Surfaces

1/ Use the *Reaction Grid* tool of AGUI to visualize the evolution of the total energy of the molecule below as a function of the two torsional angles θ1 and θ2.



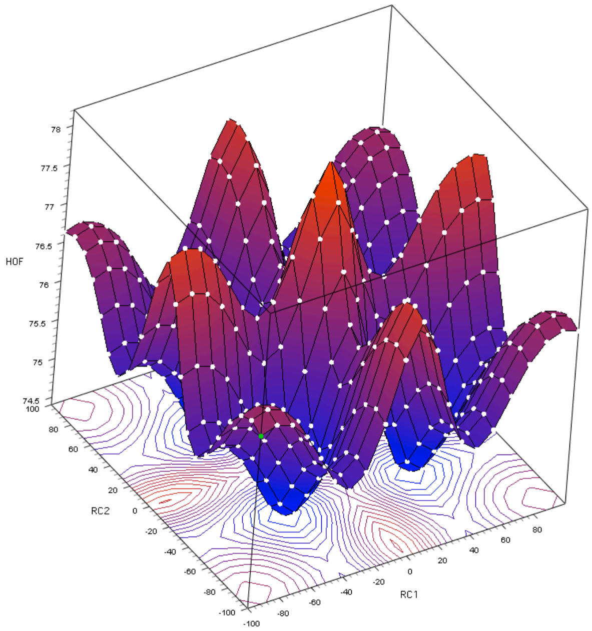
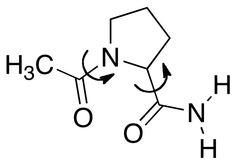


Figure 5. Evolution of the total energy of the molecule as a function of the two torsional angles.

In the explored range of θ1 and θ2, the potential energy surface exhibits minima and maxima corresponding the equilibrium and transition structures, respectively.

2/ Build the potential energy surface of the N-Acetyl Proline Amide molecule as a function of the orientation of the two substituents.



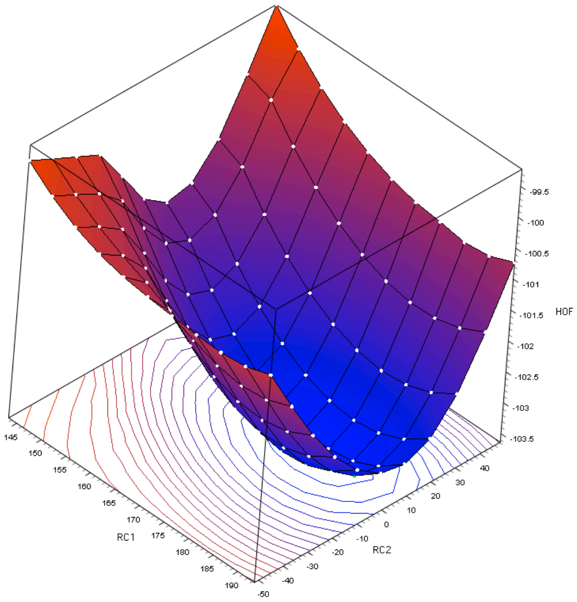


Figure 6. Evolution of the total energy of the molecule as a function of the two torsional angles.

In the explored range of $\theta 1$ and $\theta 2$, the potential energy surface exhibits one single minimum corresponding to the equilibrium structure featuring a H-bond between one of the H atoms of the amide group and the oxygen of the ether.