Experiment 3: Applying DFT to Organic Chemistry – Part A

Rotational barriers, conformers and cis–trans isomers

Tip

At a glance. 8 molecules × 16 methods = **128 jobs** with the def2-TZVP basis, from a few seconds to about 3 minutes each (the diol and pentene with hybrid meta-GGAs are the slowest). Plan to submit them in batches (see working on a shared machine). **You will learn** how methods on different rungs of Jacob's ladder perform for "easy" organic reactions, what dispersion corrections do, and what each functional costs.

Background

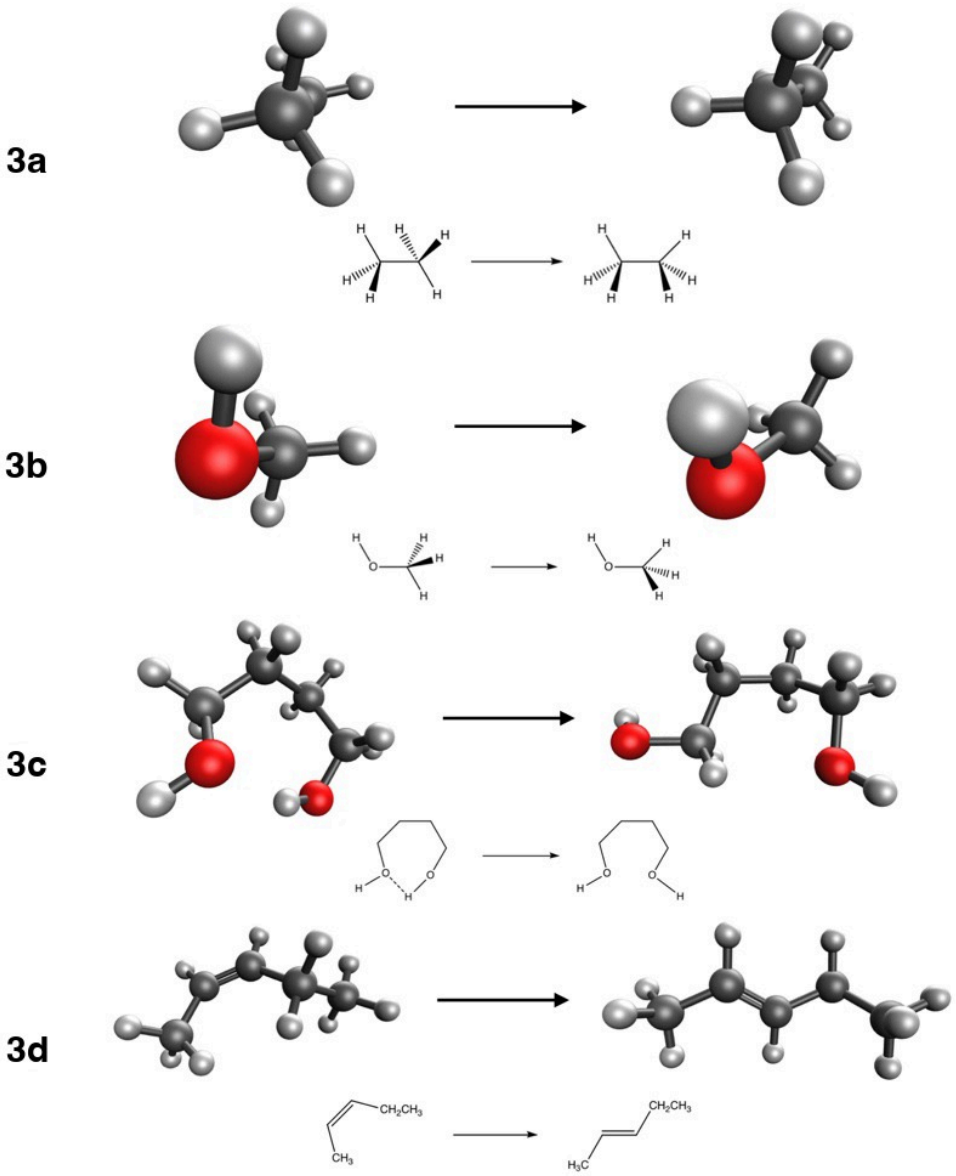


Figure 1: Reactions studied in Experiment 3: rotational barrier of ethane (3a) and methanol (3b), a conformational change of butane-1,4-diol (3c), and the cis–trans isomerization of pent-2-ene (3d). Carbon is black, oxygen red, hydrogen white; dotted lines are hydrogen bonds.

In this experiment you will analyze four reactions found in most introductory organic chemistry textbooks. For **3a** you will calculate the energy difference between the staggered and eclipsed conformations of ethane. For **3b** you will do the same for methanol. For **3c** you will look at a change of conformation in butane-1,4-diol, which breaks an intramolecular hydrogen bond. **3d** is the isomerization of *cis*-pent-2-ene to *trans*-pent-2-ene. The molecules come from the BHROT27 [1], BUT14DIOL [2] and FH51 [3], [4] subsets of the GMTKN55 database [1].

The methods are:

- **LSDA:** SPW92 [5], [6], [7]
- **GGA:** BP86 [8], [9], [10], BLYP [8], [11], PBE [12] and PBE-D4 [12], [13], [14]
- **meta-GGA:** SCAN [15] and B97M-V [16], [17]

- **hybrid GGA:** B3LYP [8], [11], [18], [19], [20], B3LYP-D4 [13], [14], B3PW91 [6], [7], [8], [19], [21] and PBE0 [22], [23]
- **hybrid meta-GGA:** M06-2X [24], M11 [25], MN15 [26] and ωB97M-V [17], [27]
- **Hartree–Fock** [28], [29], [30], [31]

Use the **def2-TZVP** basis set [32] for every calculation.

The reference energies are:

Reaction	3a	3b	3c	3d
ΔE_{ref} (kcal/mol)	2.73	1.01	3.29	−1.15

Compute each reaction energy as $\Delta E = \Sigma\ \nu_i\ E_i$, with $\nu_i > 0$ for products and $\nu_i < 0$ for reactants (units guide), then the signed error $\varepsilon = \Delta E_{comp} - \Delta E_{ref}$ and the absolute error $|\varepsilon|$.

Enter your results

For every job, record the **total energy**, the **number of SCF cycles** and the **wall time** (where to find them). The page computes the **time per SCF cycle** for you in the explore section. Then enter your reaction energies in the last tab.

We will discuss these results more extensively after Experiment 5, when you have seen “easy”, “medium” and “hard” reactions.

Go further (optional)

Note

Scan the full ethane rotation. Reaction 3a compares just two points on a curve. In this Colab notebook you rotate one methyl group from 0° to 120°, compute the whole torsional profile with PySCF, and see where the barrier comes from. Open in Colab

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