

Exercise Ex8

December 19, 2025

Student: Firstname Lastname Sciper: 000000

Please use this template to submit your answers.

If you had to modify code from the notebook, please include the modified code in your submission either as screenshot or in a

```
\begin{lstlisting}[language=Python]
\end{lstlisting}
```

environment.

You only need to include the code cells that you modified.

Note, that references to other parts of the documents aren't resolved in this template and will show as `??`. Check the text of the exercises on website for the reference

Exercise 1

Does the bond length of the $H_3CH_2C - CH_2CH_3$ bond fluctuate as the dihedral is changed? Why (not)?

The bond length of the central $H_3C - CH_2 - CH_2 - CH_3$ bond (i.e. the C–C bond between the two methylene groups) does not show any significant fluctuation as the dihedral angle is varied. In our scan the $C - C$ distance remains essentially constant (deviations are of order 10^{-12} \AA), as shown by the flat bond length behaviour against the dihedral angle.

This behaviour is what we are expecting because we performed a rigid PES scan and not a relaxed one, in which we would have had optimized geometry for each dihedral angle, changing the bond length. The geometries along the scan are generated from a Z-matrix in which the $C - C$ bond length and all bond angles are kept fixed at their optimized values from our first step. In the end only the dihedral angle is changed. For each value of the dihedral we compute a single-point energy without further any optimization, so the $C - C$ distance cannot relax and therefore does not vary significantly with the torsion. The small fluctuations that we are observe are due to numerical noise.

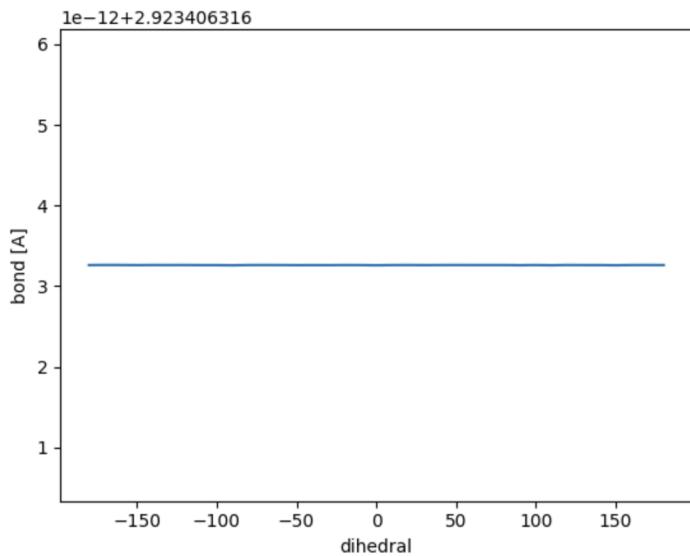


Figure 1: Bond length of the $H_3CH_2C - CH_2CH_3$ bond against dihedral angle

Exercise 2

Create a potential energy profile along the dihedral by plotting the energies of the system as a function of the scanned dihedral angle as done above. Then, to each maximum and minimum, assign the corresponding conformation from your trajectory. Show these conformations in your report. Assign also names to the conformations according to the *Newman projections* you know from organic chemistry (where possible).

The answers on Newman projections are in the caption of the figure...

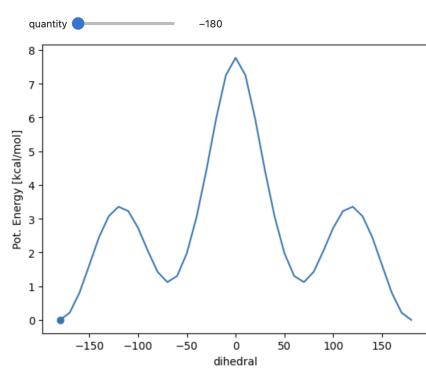


Figure 2: PES against dihedral angle at local minimum of -180 degrees

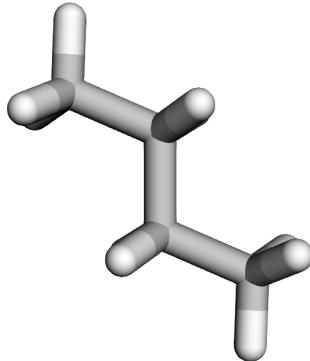


Figure 3: Molecule conformation at dihedral angle at local minimum of -180 degrees

Figure 4: Local minimum at dihedral angle of -180 degrees. Its Newman projections corresponds to : Staggered Anti

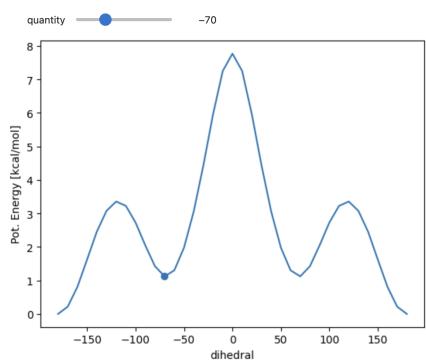


Figure 5: PES against dihedral angle at local minimum of -70 degrees

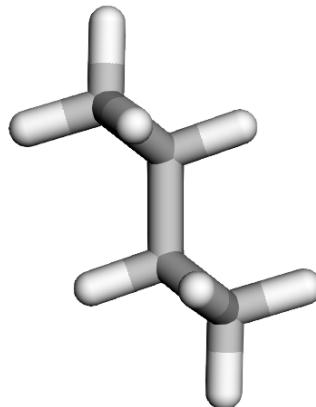


Figure 6: Molecule conformation at dihedral angle at local minimum of -70 degrees

Figure 7: Local minimum at dihedral angle of -70 degrees. Its Newman projections corresponds to : Staggered Left ($g+$)

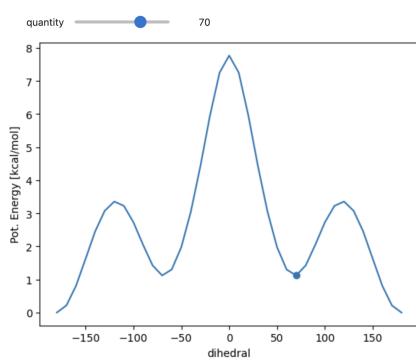


Figure 8: PES against dihedral angle at local minimum of 70 degrees

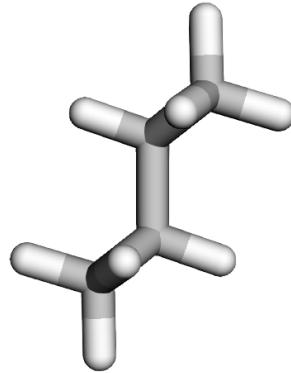


Figure 9: Molecule conformation at dihedral angle at local minimum of 70 degrees

Figure 10: Local minimum at dihedral angle of 70 degrees. Its Newman projections corresponds to : Left Staggered (*g-*)

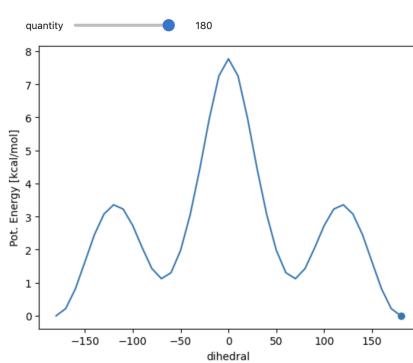


Figure 11: PES against dihedral angle at local minimum of 180 degrees

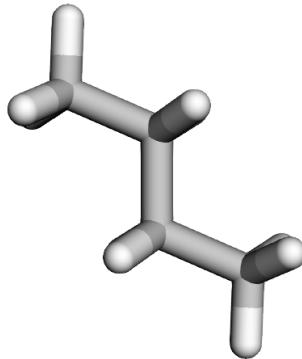


Figure 12: Molecule conformation at dihedral angle at local minimum of 180 degrees

Figure 13: Local minimum at dihedral angle of 180 degrees. Its Newman projections corresponds to : Staggered Anti

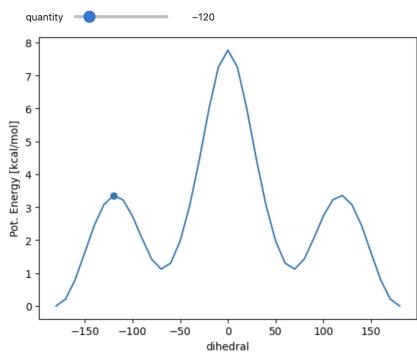


Figure 14: PES against dihedral angle at local maximum of -120 degrees

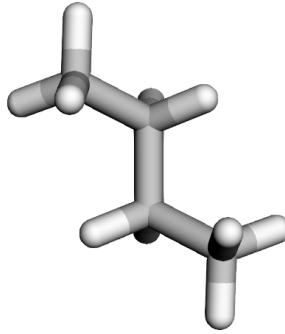


Figure 15: Molecule conformation at dihedral angle at local maximum of -120 degrees

Figure 16: Local maximum at dihedral angle of -120 degrees. Its Newman projections corresponds to : None, since the angle between front and back methyl is more than 60 degrees

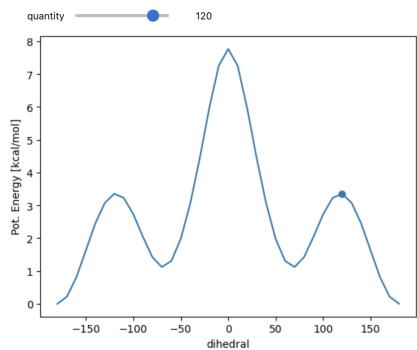


Figure 17: PES against dihedral angle at local maximum of 120 degrees

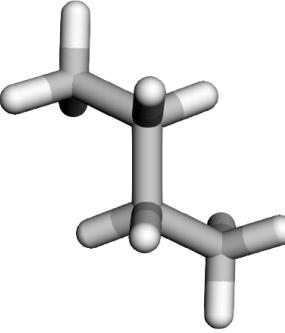


Figure 18: Molecule conformation at dihedral angle at local maximum of 120 degrees

Figure 19: Local maximum at dihedral angle of 120 degrees. Its Newman projections corresponds to : None, since the angle between front and back methyl is more than 60 degrees

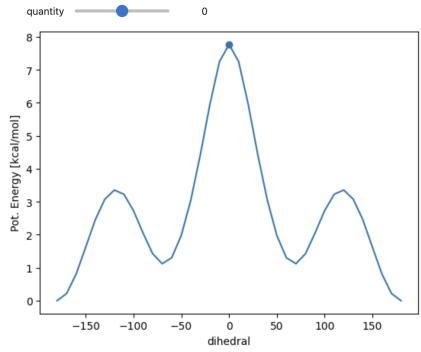


Figure 20: PES against dihedral angle
at local maximum of 0 degrees

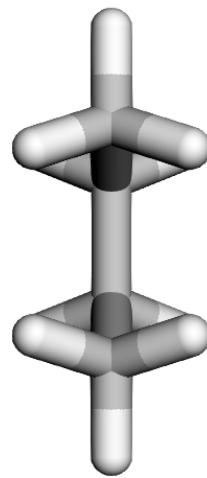


Figure 21: Molecule conformation at
dihedral angle at local maximum of 0
degrees

Figure 22: Local maximum at dihedral angle of 0 degrees. Its Newman projections corresponds to : Eclipsed

Exercise 3

The rotational barrier of butane lies between 5 and 6 kcal mol⁻¹ [Murcko1996]. Compare this value with the one you calculated and explain possible sources of error, leading to higher or lower barriers.

From the rigid scan of the central $C - C$ dihedral we obtain a maximum relative energy of

$$\Delta E_{\text{rot}}^{\text{calc}} \approx 7.768976939114509 \text{ kcal mol}^{-1},$$

between the global minimum (anti conformation at $\phi \approx 180^\circ$) and the eclipsed conformation ($\phi \approx 0^\circ$). This value is somewhat higher than the literature barrier of 5–6 kcal mol⁻¹ for butane ¹

We can think of several approximations in our calculation that can explain this difference:

- Rigid Scan : where in the PES scan all internal coordinates except the dihedral were kept fixed at their optimized values. The molecule cannot relax (for example slight changes in $C - C$ and $C - H$ bond lengths and angles) as it is twisted, which artificially increases the energy of the eclipsed conformations and therefore tends to overestimate the rotational barrier.
- DFT method used : indeed we took the BLYP/6-31+G* DFT model, this is a GGA functional with a relatively modest basis set. Torsional barriers are sensitive to the quality of the exchange correlation treatment and basis set; higher-level methods (hybrid functionals) usually yield to more accurate barriers.
- Missing vibrational/thermal corrections. Our scan is based on pure electronic energies at 0 K. The quoted 5–6 kcal mol⁻¹ barrier typically includes zero-point vibrational energy and, to some extent, finite-temperature effects, which can lower the effective barrier due to leakage.
- Discretisation of the scan : The dihedral was sampled every 10° , so the true maximum may lie between grid points. This effect is small here but introduces an additional numerical errors.

¹Murcko *et al.*, J. Phys. Chem. **100**, 16162 (1996).