DP4+ App

https://github.com/Sarotti-Lab/DP4plus-App

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Example Manual - Custom-DP4+ - Train

Overview

The DP4+App is designed to facilitate the correlation of experimental NMR chemical shifts with DFT magnetic tensors. *This manual outlines the process of training a **Custom-DP4+** theory level.*

While DP4+App features 60 pre-parameterized theory levels spanning DP4+ and MM-DP4+, it also offers the capability to train custom levels according to user preferences. The recommended procedure outlined was developed in our group[1] and involves the use of eight molecules for which experimental data is provided. By following this detailed process, you can train a new theory level and gain a comprehensive understanding of the underlying mechanics for future customizations.

Content

The "*example_custom_training / Train"* folder contains the following components:

- *Training calculations*: In the "*Train"* folder, twenty-one '*.log*' files provide NMR calculations for the eight depicted molecules. Previous structure optimization was carried out with MMFF force field, followed by calculations using the Gaussian 09 command:

```
# mPW1PW91/6-31g** scrf=(pcm,solvent=chloroform,smd,dovacuum) nmr
```

- *Correlation spreadsheet: custom_corrleation_file.xlsx* comprises the experimental chemical shifts for each molecule in different sheets. This file also incorporates correlation labels establishing a correspondence between experimental and computational models.

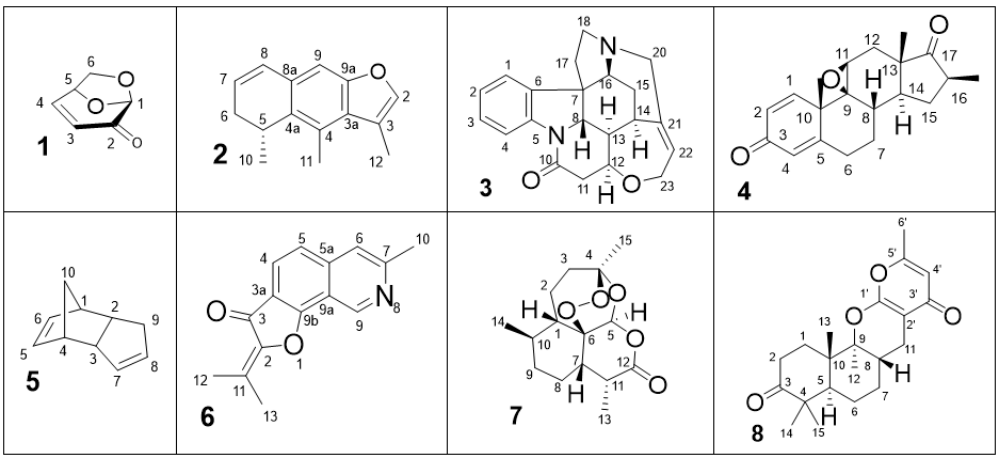


Table 1. Training set molecules with experimental labels.

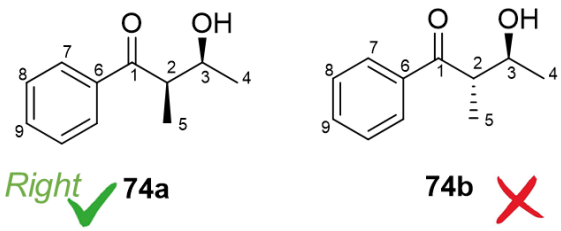
[1] **Zanardi, M. M., & Sarotti, A. M. (2021).** *Sensitivity analysis of DP4+ with the probability distribution terms: Development of a universal and customizable method*. The Journal of Organic Chemistry, 86(12), 8544-8548.

The "*example_custom_training / Calc*" folder contains the following components:

- *Training calculations*: In the "*Calc*" folder, twenty-six '*.log*' files provide NMR calculations for the two depicted isomers. Previous structure optimization was carried out with MMFF force field, followed by calculations using the Gaussian 09 commands:

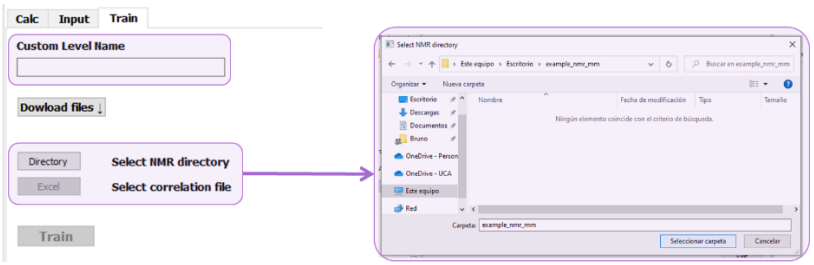
```
# mPW1PW91/6-31g** scrf=(pcm,solvent=chloroform,smd,dovacuum) nmr
```

- *Correlation spreadsheet: 74a_correlation.xlsx* comprises the experimental chemical shifts for the isomer 74a (the right one). This file also incorporates correlation labels establishing a correspondence between experimental and computational models.

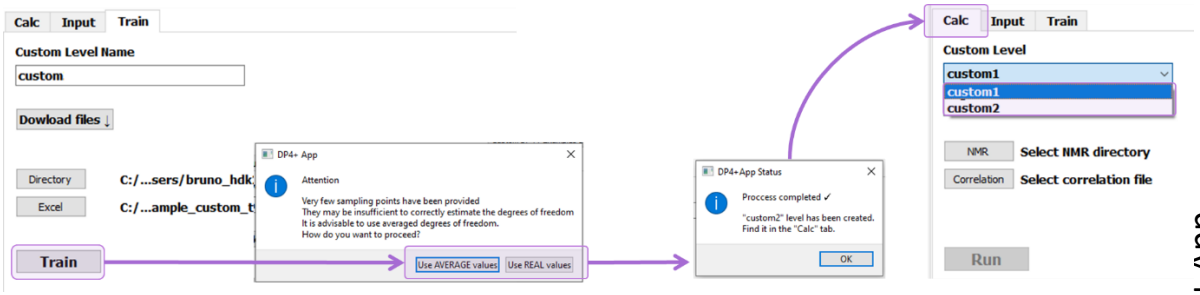


Procedure

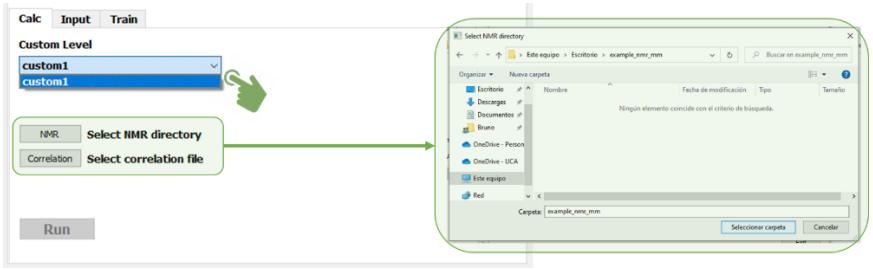
To begin, open the **Train** tab and assign a valid name in the frame. It must be lowercase and contain no special characters. Then utilize the designated buttons situated beneath to select the folder and spreadsheet in this example. DP4+App will validate the data to ensure compatibility with the procedure. Please consult the User Manual's *'Warnings and Input Control*' section for specific requirements. The status bar will guide you through the procedure.



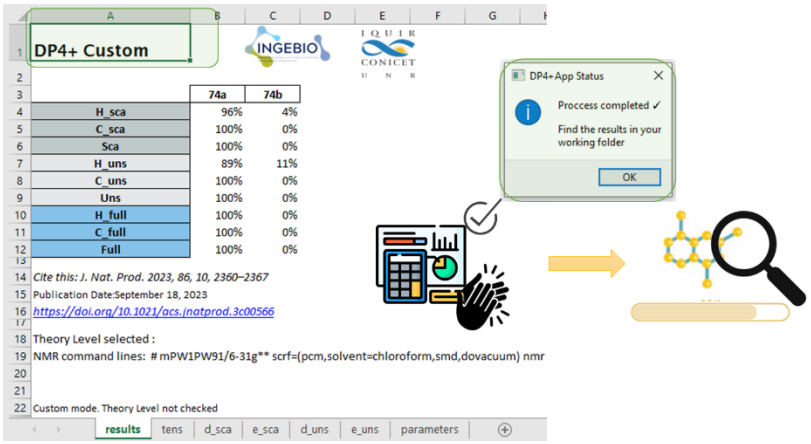
Given the limited number of molecules in this example, DP4+ provides the option to replace the calculated degrees of freedom with averaged values from known distributions. The use of averaged values is recommended, as they have been shown to better fit in small parameterization sets.[1]



A pop-up will signal the successful training completion and the new level will be available in the **Calc** tab. To test the level in a DP4+ calculation, select the trained level in the dropdown list and the given files in the *Calc* folder.



The computed data will be stored in the file *'CustomDP4plus_results.xlsx'* located in the working directory. The calculation is now finished, allowing you to begin your analysis.



Disclaimer

This example is provided for educational purposes only to illustrate the application's capabilities. The analysis is not based on real-world data. To simplify distribution, not all conformations within a 10 kcal/mol energy window are included in this example. Therefore, replicating this study may produce varying outcomes.