Imperial College London

Investigation of Reorganisation Energies in Organic Molecules using Computational Methods

Kye Bong Choo
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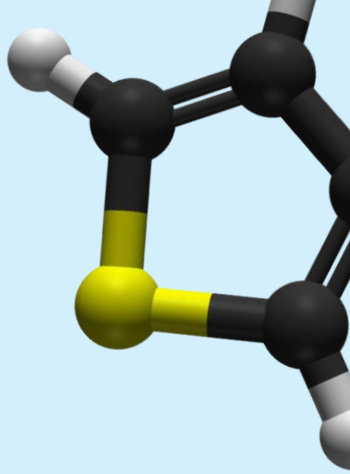
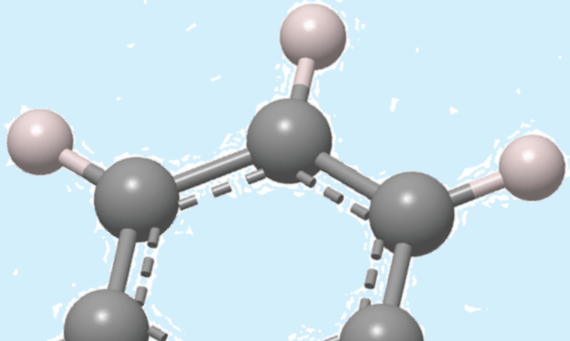
Prof. Jenny Nelson
Dr Mohammed Azzouzi





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Motivation*: Why this is worth the effort

- Road to net zero. Rare earth materials are expensive and scarce.
- Organic semiconductors could be a good alternative.
- Many possible structures to evaluate.

Issues with evaluating organic semiconductors:

- Computationally demanding.
- Slow to calculate and there's many ways to extend the organic molecule starting from a single benzene.

What if there's a faster way to perform the analysis? Could we implement machine learning methods to help guide us in our evaluation of organic semiconductors?

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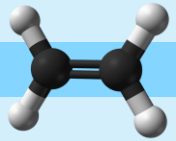
Brief Overview:



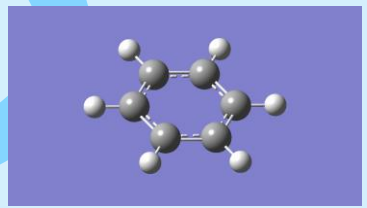
Molecule Creation

RDKit

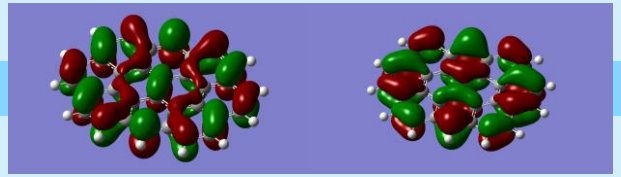
Geometry Optimisation

Expanding the limits of computational chemistry

Vibrational Mode Analysis

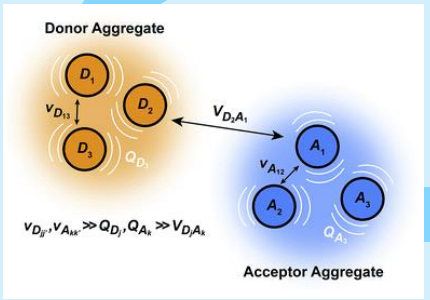


Orbital Analysis



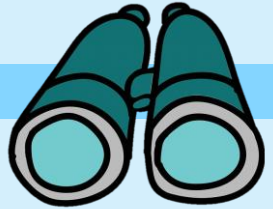
*Ovalene: Left = Anion HOMO; Right = Ground HOMO

Energy Analysis



[1] charge transfer between two delocalised aggregates

Interpret and Repeat



[1] Generalised Marcus Theory for multi-molecular delocalised charge transfer, Natasha B. Taylor & Ivan Kassal.

2 min

Investigation of Reorganisation Energies in Organic Molecules using Computational Methods

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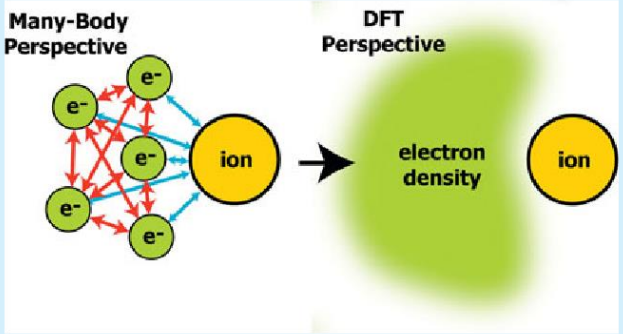
Objectives:

- Investigate how reorganisation energies change with molecule structure.
- Design a high throughput method to evaluate larger sets of molecules.
- Identify main features that impacts the reorganisation energy of a molecule and its relationship to the HOMO and LUMO levels of the molecule.

Optimisation: Density Functional Theory



[2] DFT approximates the interaction between parts in a molecule by swapping out the electrons with an electron density region.

Electron-nuclei interaction

Correction for unwanted self-interaction

$$E = \boxed{-\frac{1}{2}\sum_{i=1}^{N}\langle\phi_i|\Delta\phi_i\rangle} + \boxed{\int v(r)\rho(r)dr} + \boxed{\frac{1}{2}\iint\frac{\rho(r_1)\rho(r_2)}{|r_1-r_2|}dr_1dr_2} + \boxed{E_{xc}[\rho]}$$

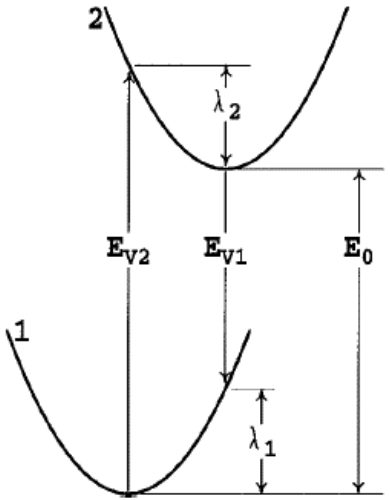
Electron kinetic energy

Electron cloud self-interaction

[3] More intuitive explanation of DFT.

[2] High-performance computing for materials design to advance energy science, Mark T. Lusk.
[3] Ideas of Quantum Chemistry, Lucjan Piela.

Vibration and Energy: Marcus & DUSHIN



[4] Given molecular potential surfaces 1 and 2, E_{V1} and E_{V2} are the vertical excitation energies, E_0 is the adiabatic energy difference, and the reorganization energies is given by λ_1 λ_2.

4-point method: $D^- + A \rightarrow D + A^-$

Reorganisation energy (DUSHIN):

$$\lambda_{total} = \sum_{i=1}^{n} \lambda_i = \sum_{i=1}^{n} \frac{h}{2} v_i \delta_i^2$$

Geometry change projected in direction of normal modes

Energy of each vibrational mode

Vibration frequency

Transition Rate:

$$k = He^{-\frac{(\Delta G_0 + \lambda)^2}{4\lambda k_B T}}$$

Dependence on electronic coupling

[4] A practical method for the use of curvilinear coordinates in calculations of normal-mode-projected displacements and Duschinsky rotation matrices for large molecules, Jeffrey R. Reimers.

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Workflow: Scaling Up

Python (Local)

Research Computing Service **HPC**

1. Input molecule using Simplified Molecular Input Line Entry System ('SMILES')
2. Using RDKit, perform a first round MMFFO before generating coordinates
3. Job files (.gjf and .sh) are submitted to the HPC to run an optimisation and frequency calculation
4. Optimised ground state geometries are used to create the job files for the charge/excited state geometries.
5. The same job is done for the charged/excited state
6. Output files are read to obtain the vibrational modes and also the HOMO-LUMO levels of the molecule
7. Using the output files from the Gaussian optimisation, DUSHIN takes the coordinates and vibrations and computes the Reorganisation Energy

Gaussian16

DUSHIN

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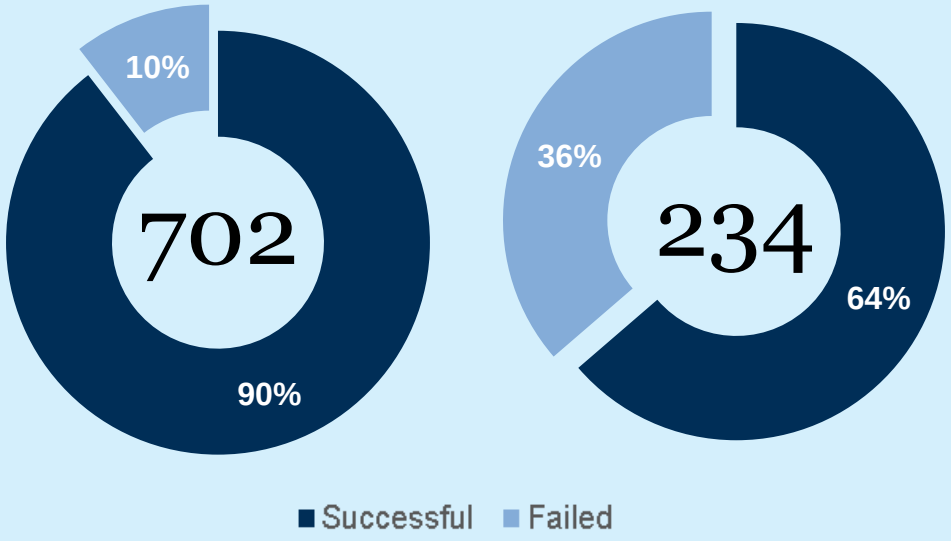
Preview of Data Set:

Total Gaussian16 optimisations ran over past 4 weeks: **1404** allowing us to compute over **702** transitions for **234** molecules



Selection Criteria

- Oligophenes and thiophenes,
- ‘Linear’ molecules first,
- On PubChem [5], export most similar structures based on Tanimoto distance;
- Possible issue with molecule validity as criteria for publishing not clear.

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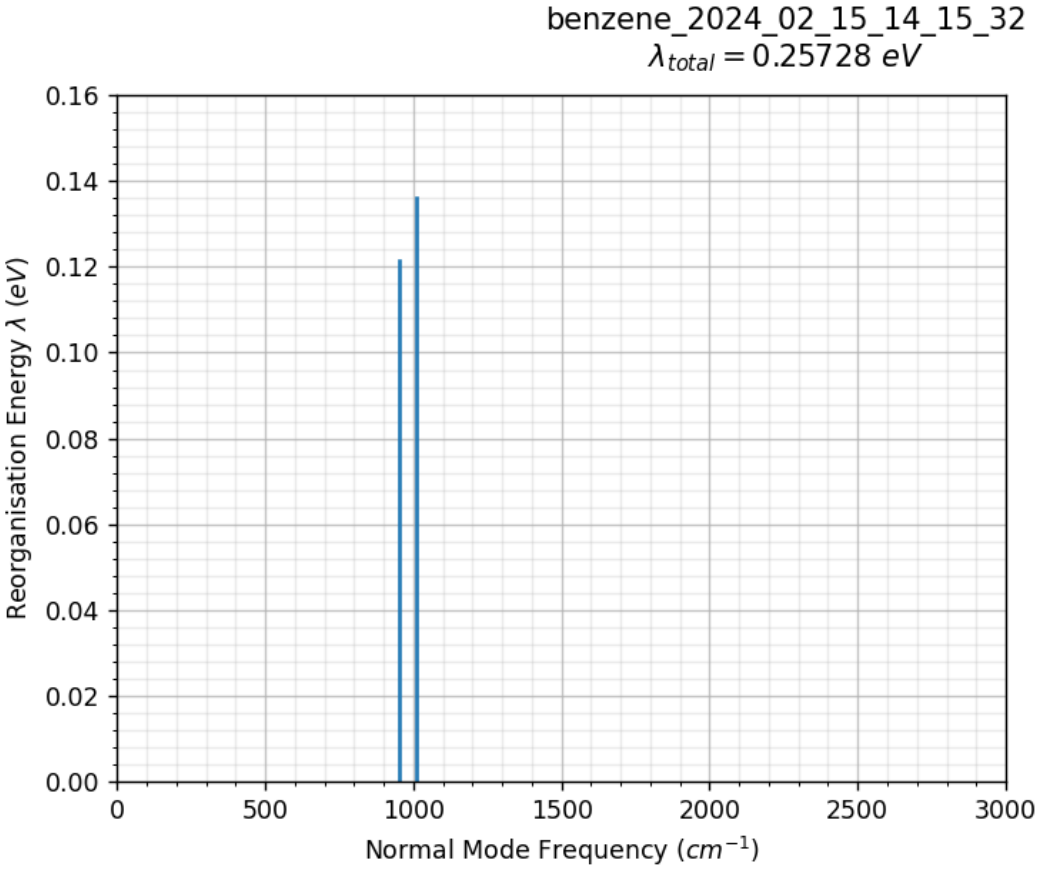
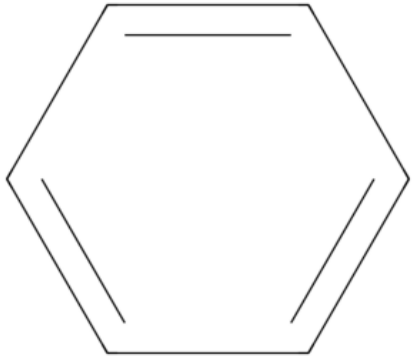
Preview of results:





Speed Run

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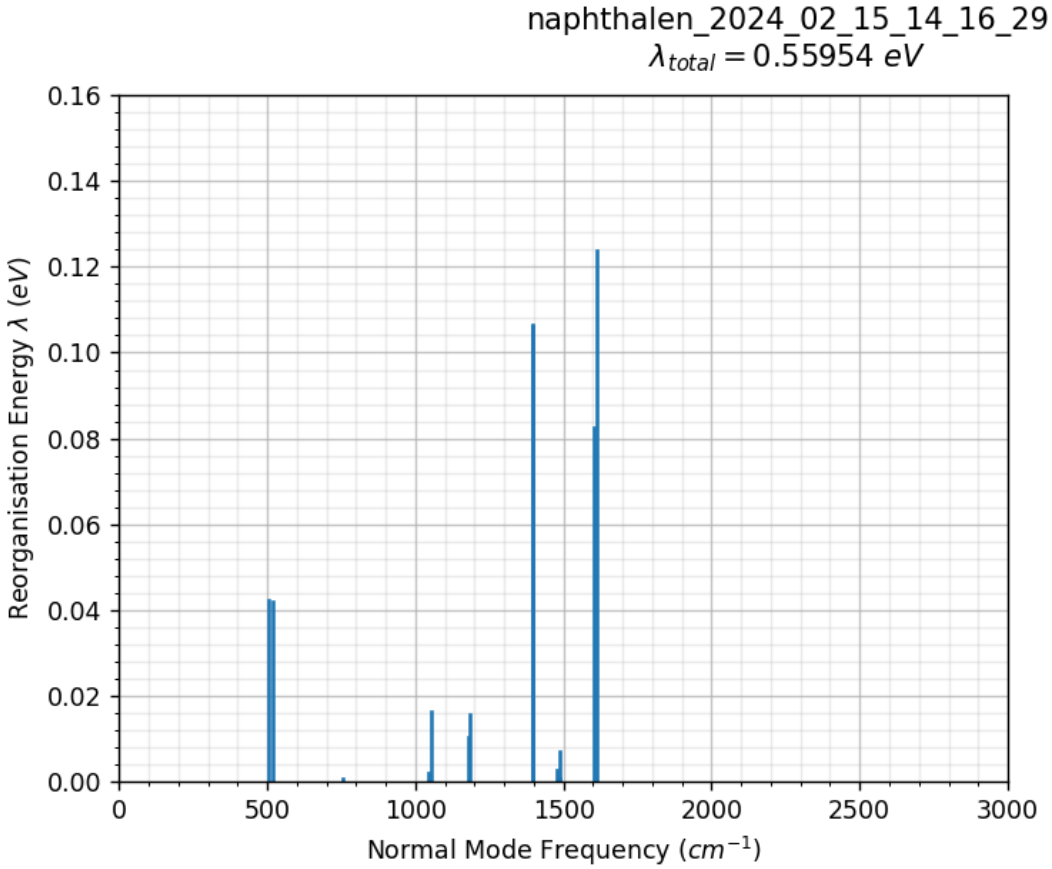

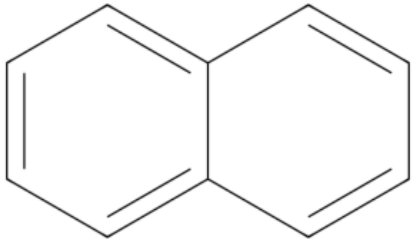

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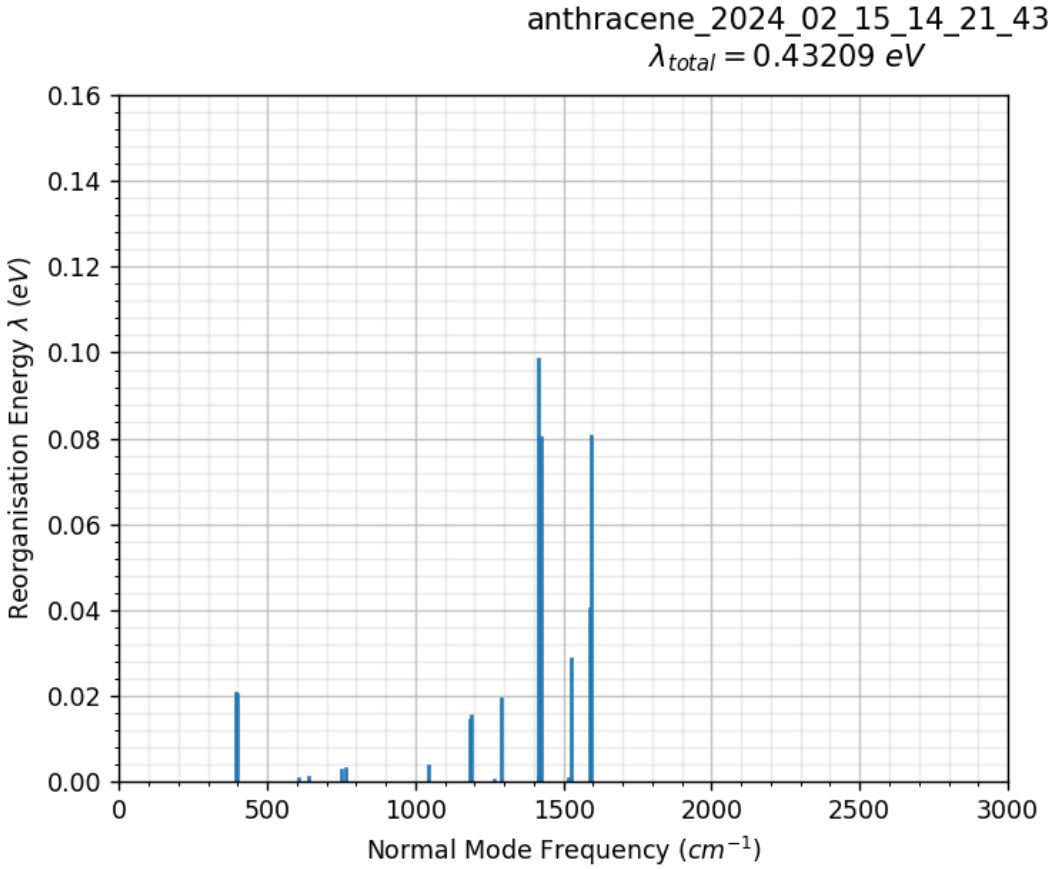

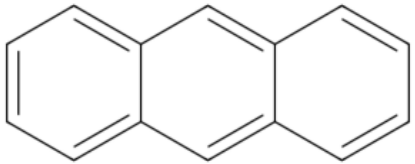

Speed Run

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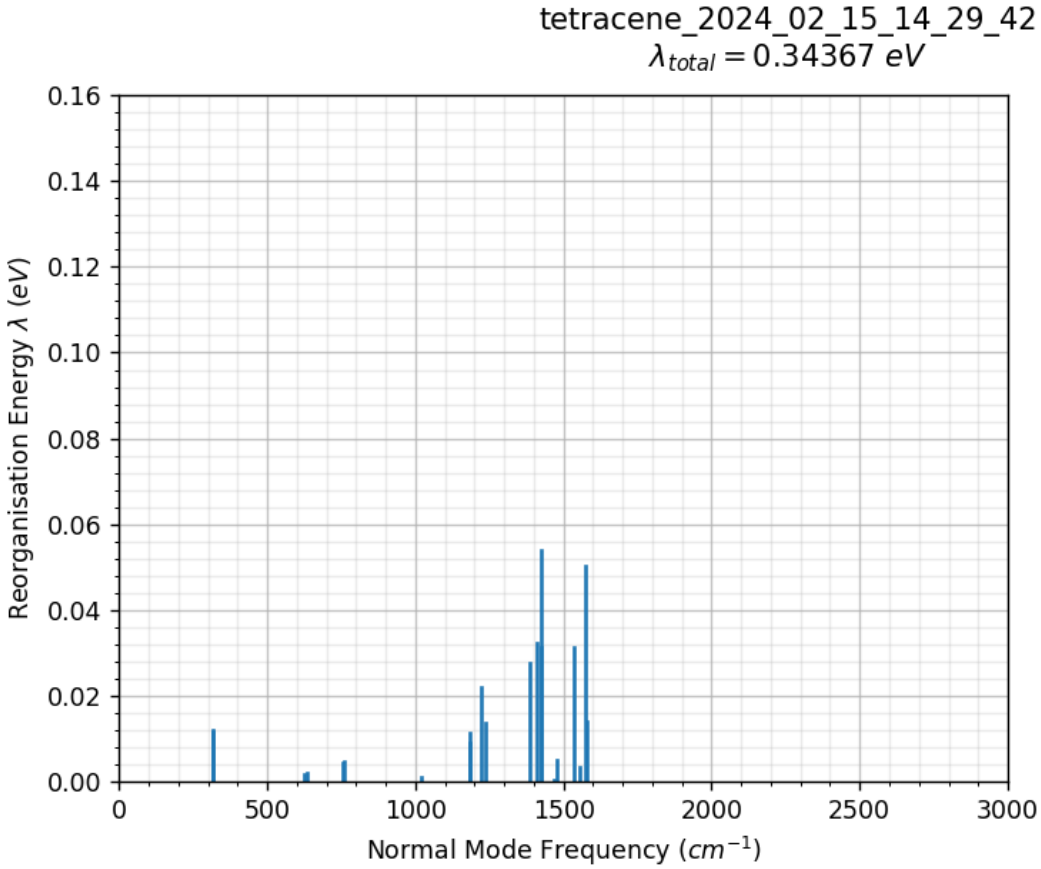

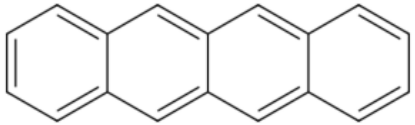

Speed Run

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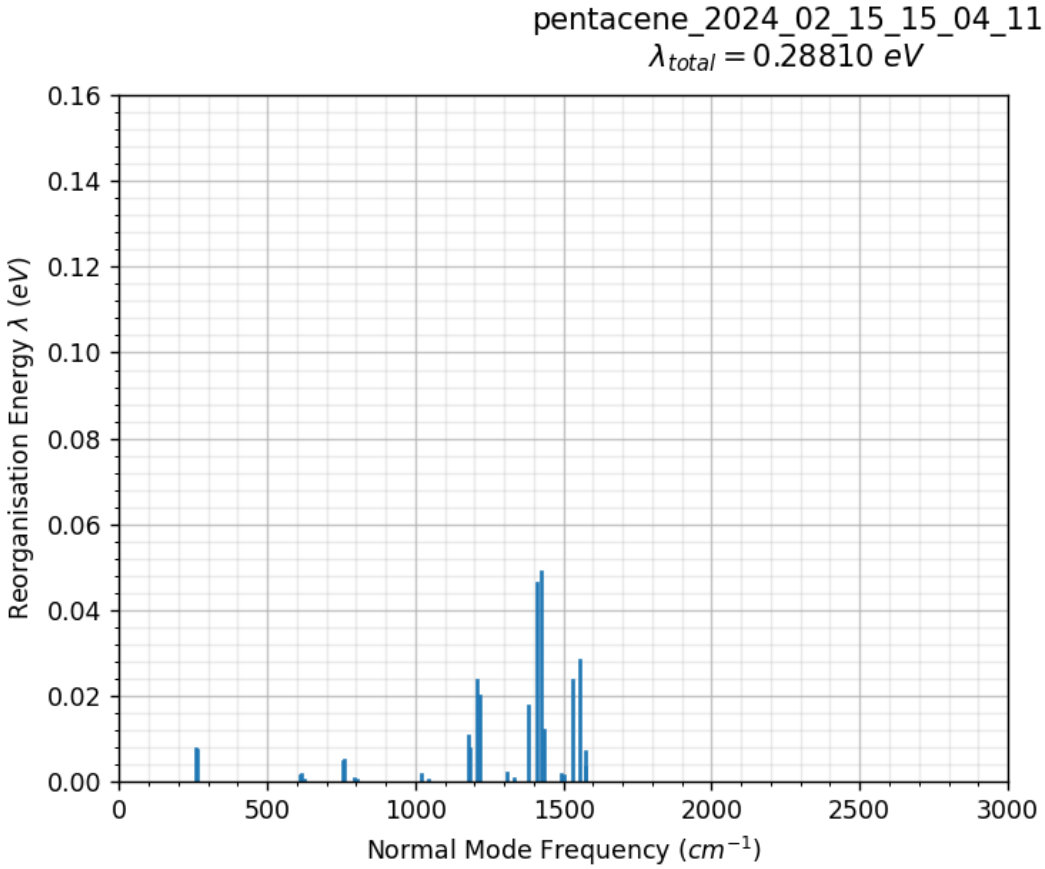

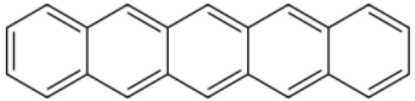

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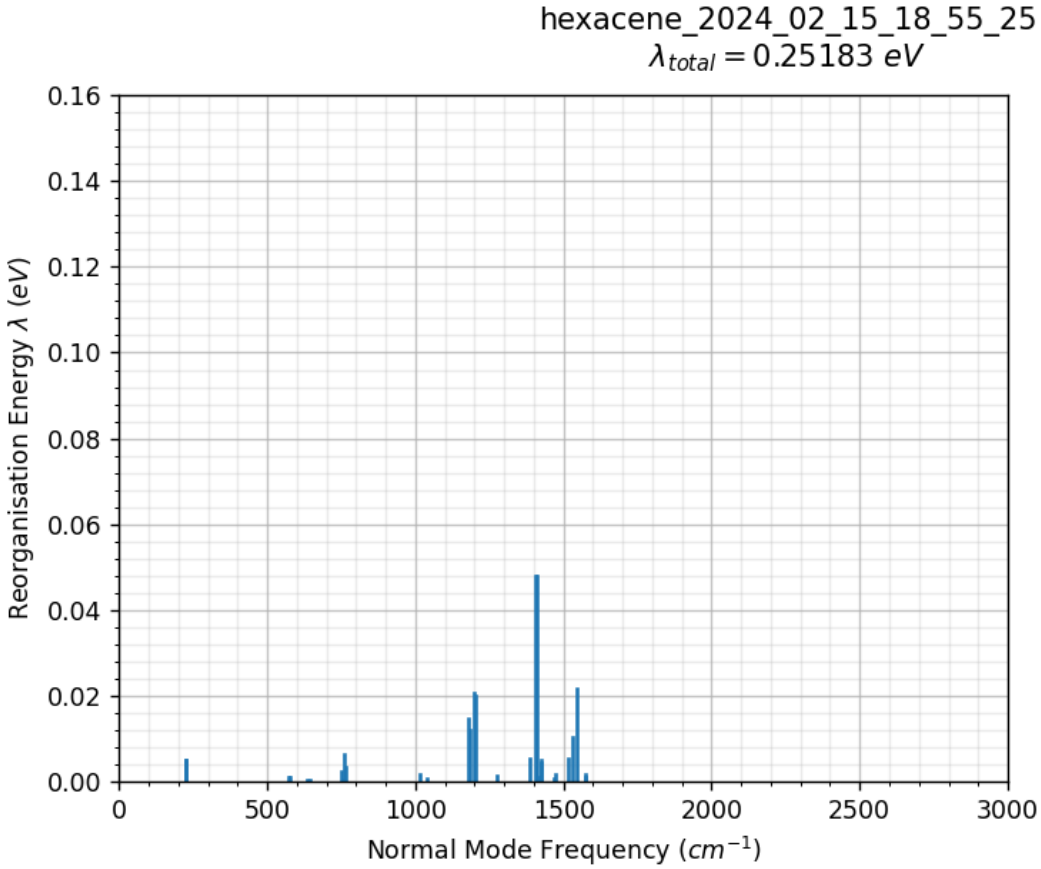

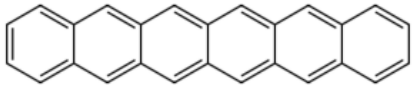

Speed Run

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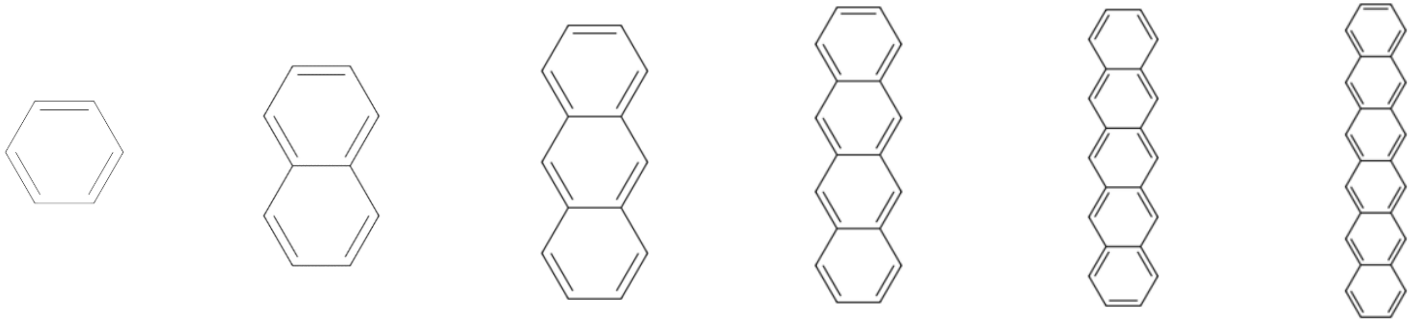
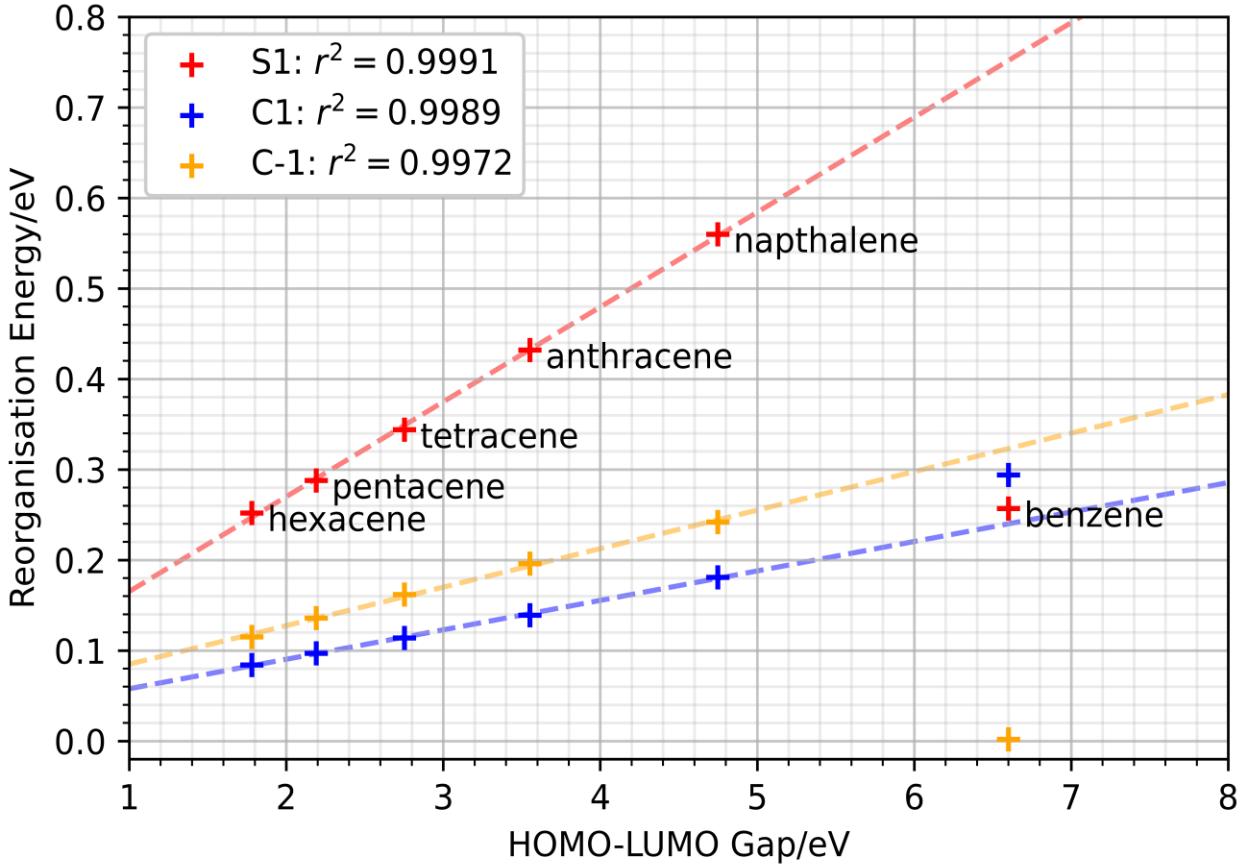
Preview of results: Dependence on Cyclic Number



Molecule	Benzene	Napthalene	Anthracene	Tetracene	Pentacene	Hexacene
S0 to S1	0.257	0.560	0.432	0.344	0.288	0.252
C0 to C1	0.294	0.181	0.139	0.114	0.097	0.084
C0 to C-1	0.002*	0.242	0.196	0.162	0.136	0.115
HOMO-LOMO Gap	6.600	4.748	3.552	2.752	2.190	1.780

Preview of results: Dependence on Cyclic Number



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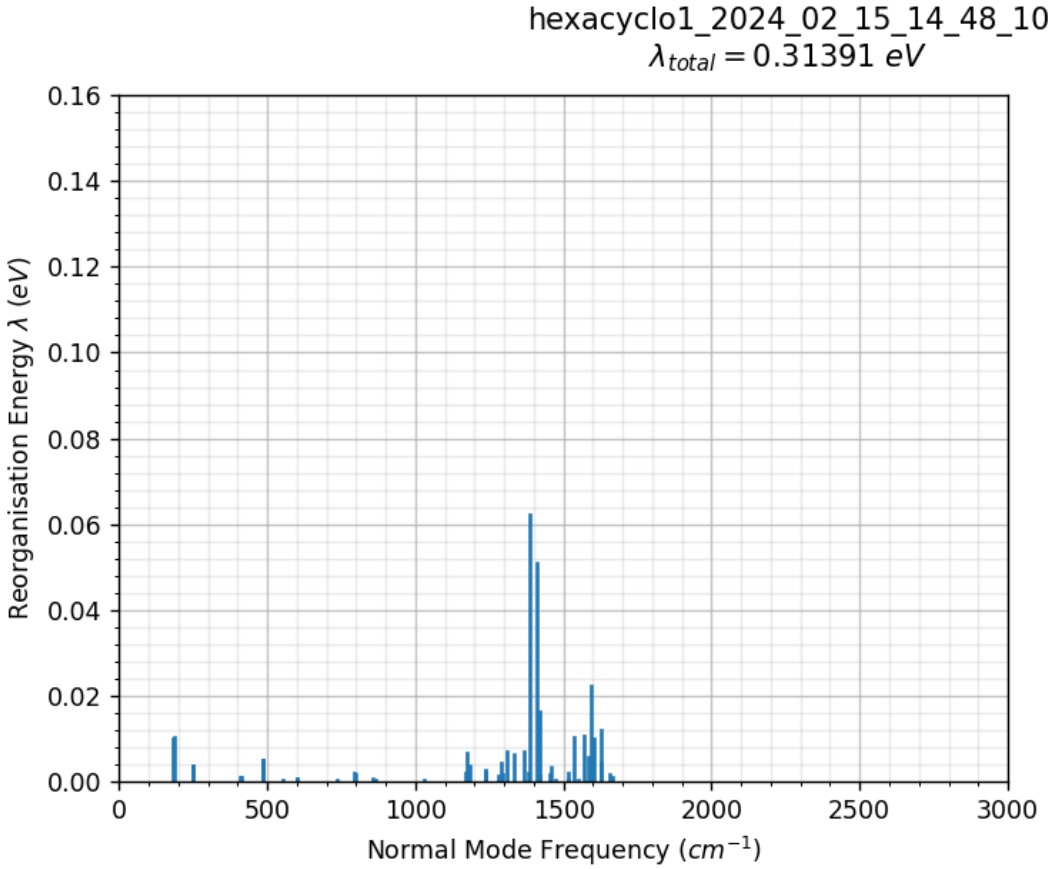

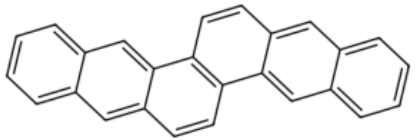

Speed Run

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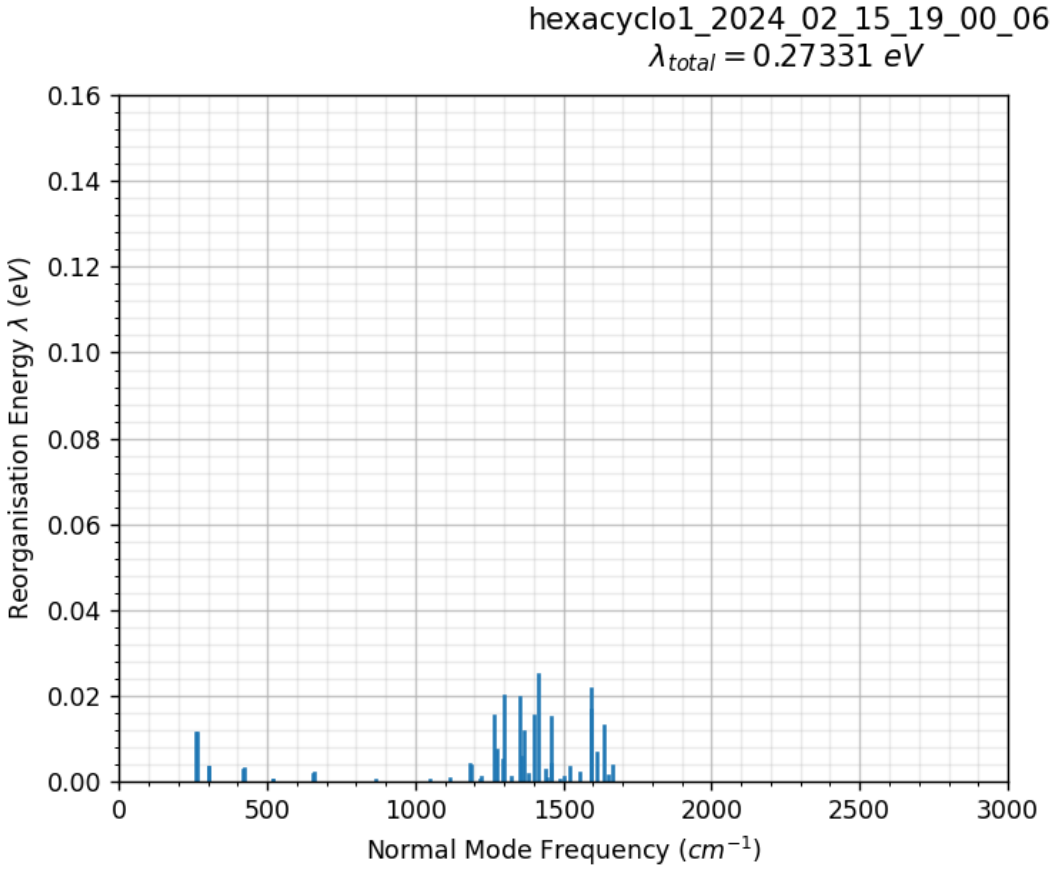

Speed Run

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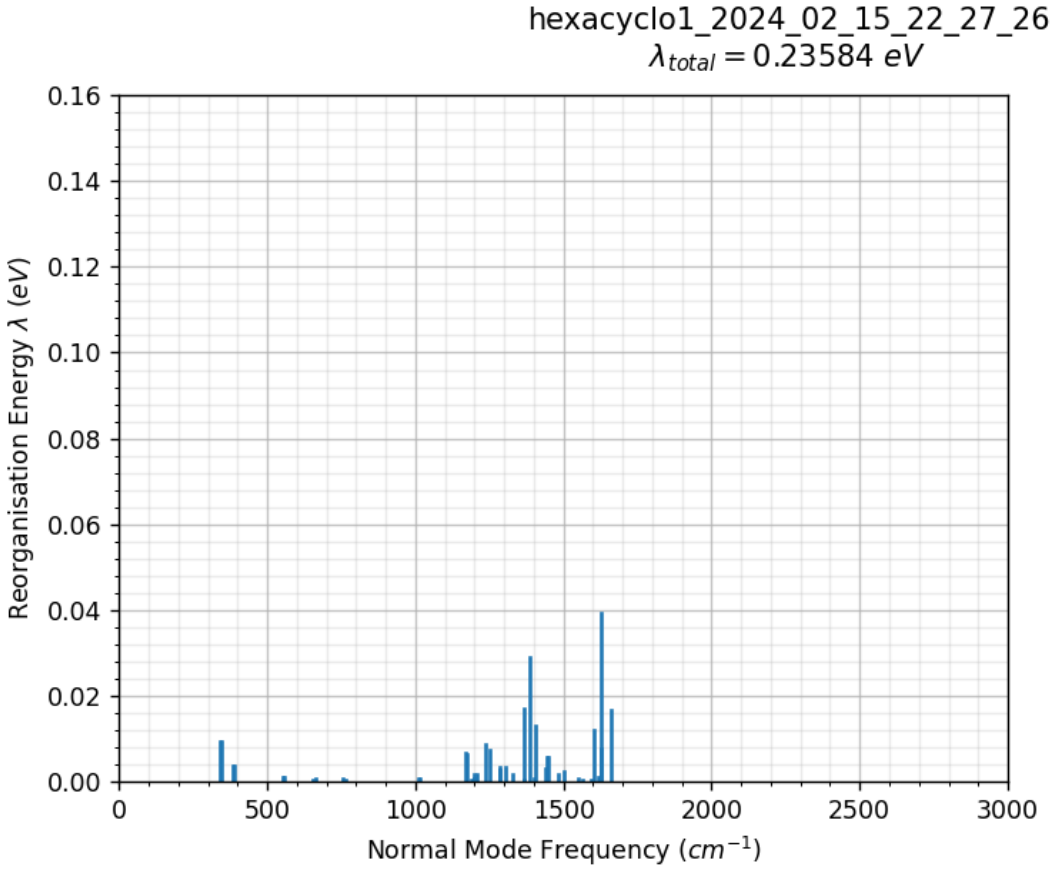

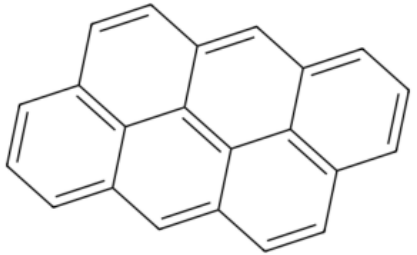

Speed Run

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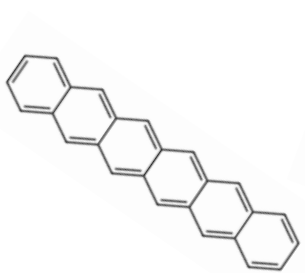
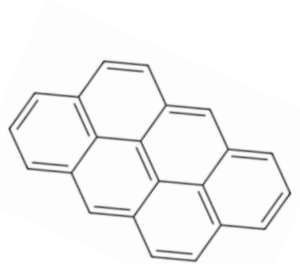
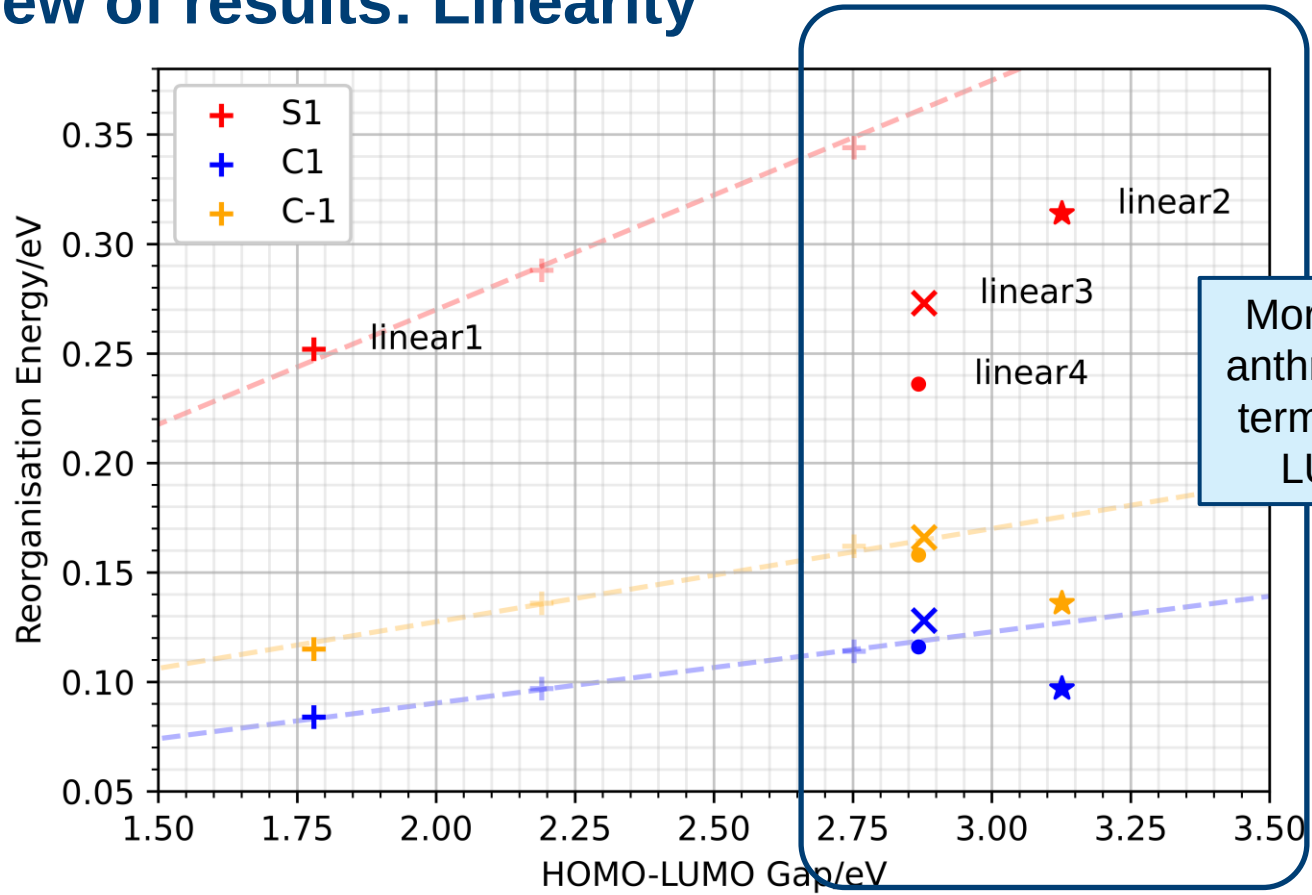
Preview of results: Linearity



S0 to S1	0.252	0.314	0.273	0.236
C0 to C1	0.084	0.097	0.128	0.116
C0 to C-1	0.115	0.136	0.166	0.158
HOMO-LOMO Gap	1.780	3.126	2.878	2.868

Preview of results: Linearity



More tetracene/ anthracene-like in terms of HOMO-LUMO gaps

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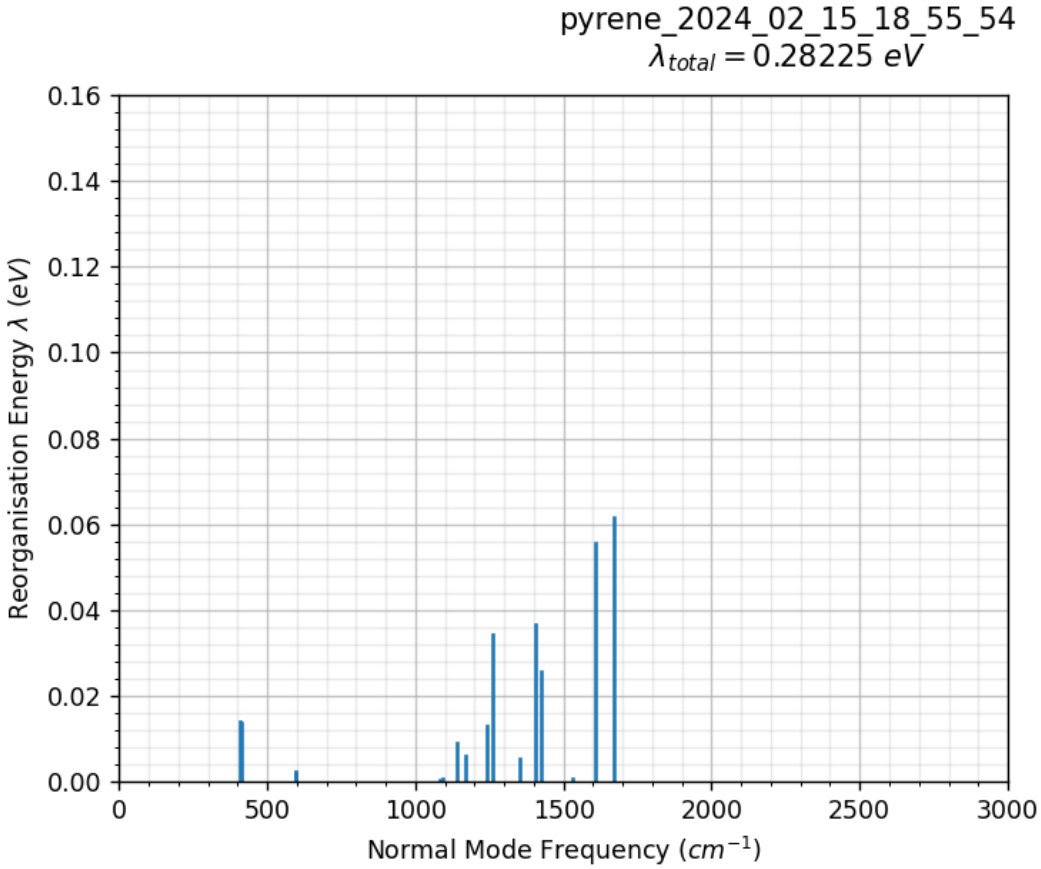
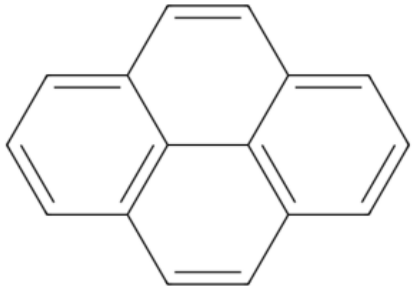
Preview of results:





Speed Run

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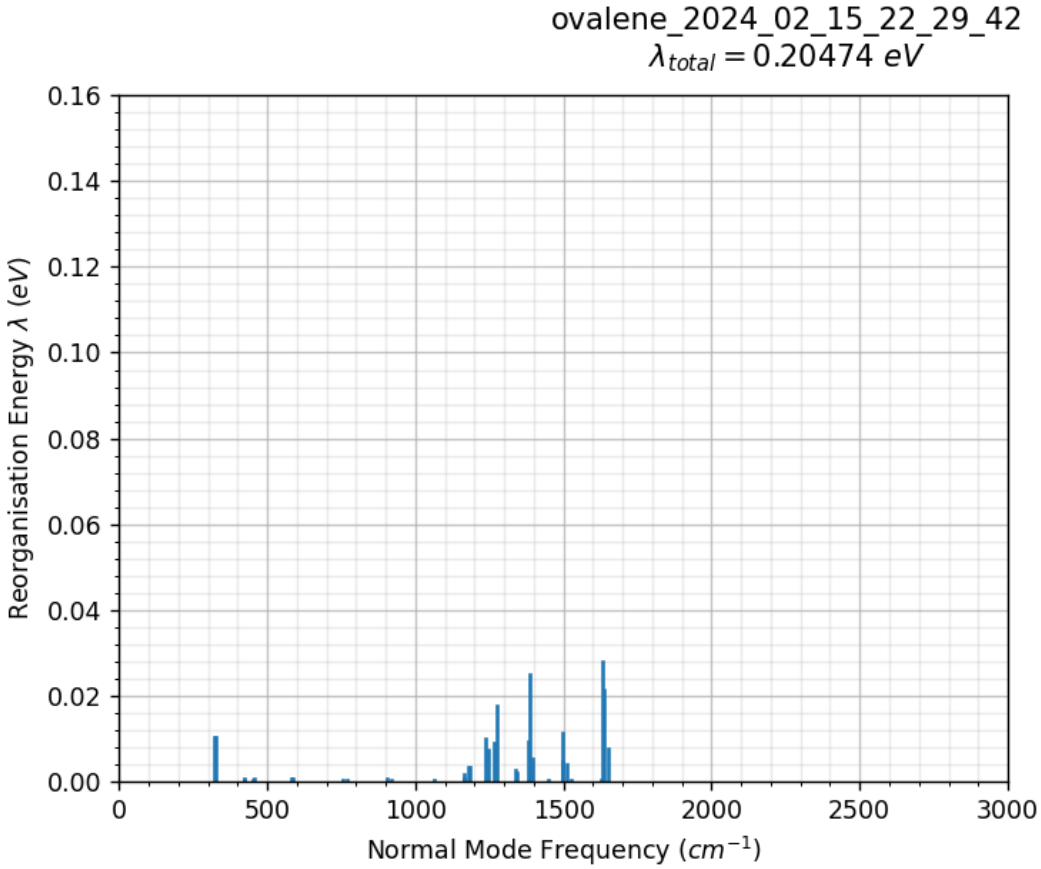

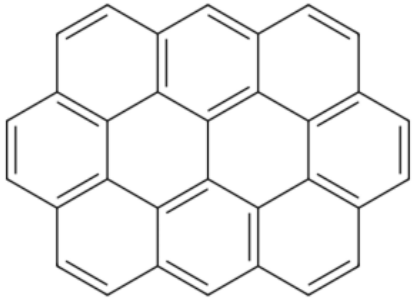

Speed Run

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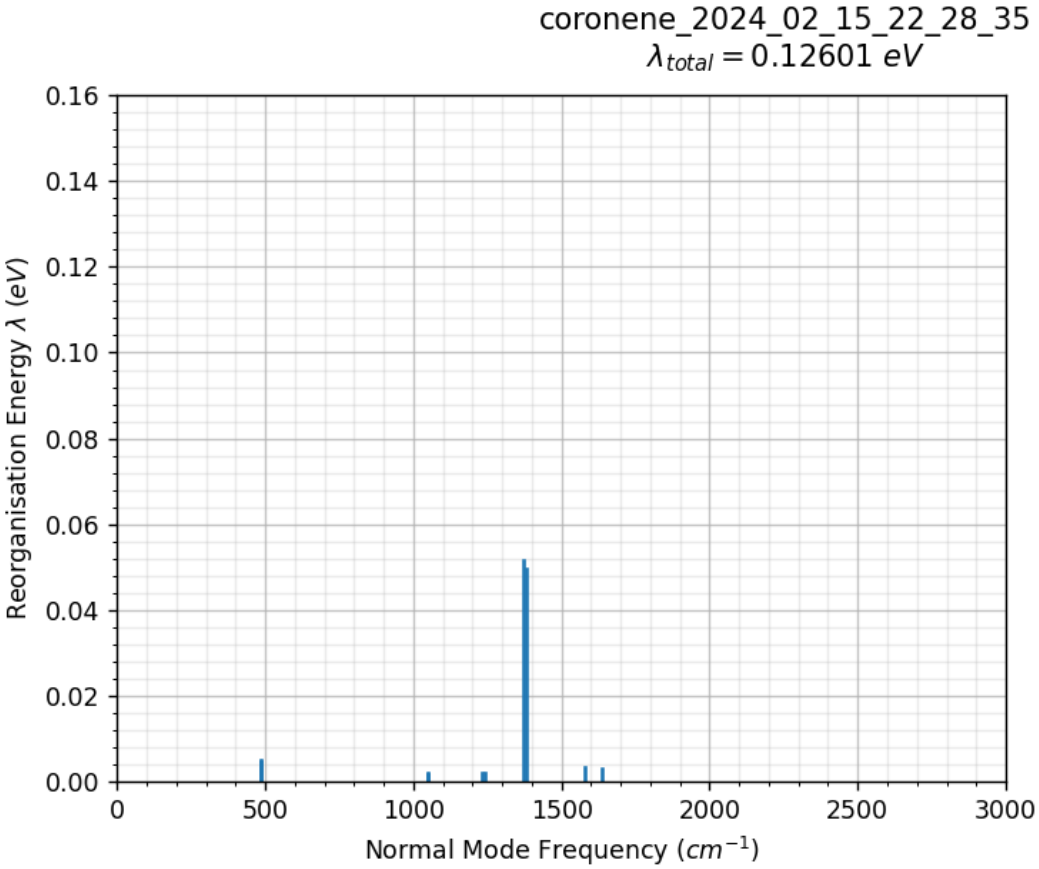

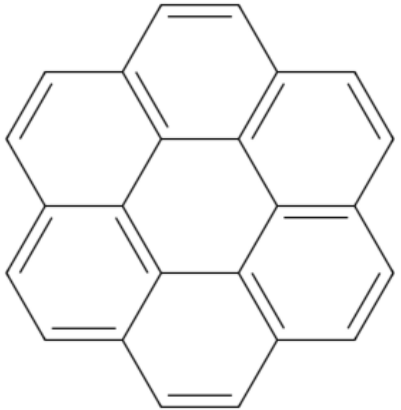

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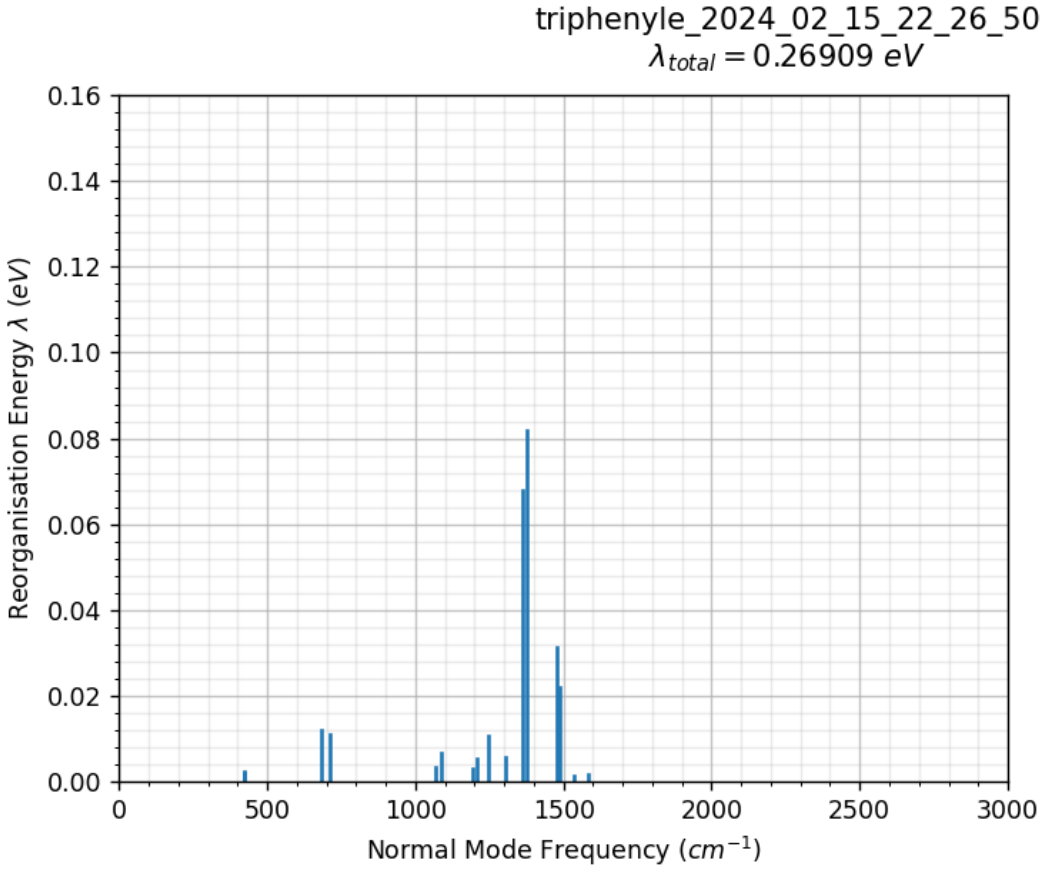

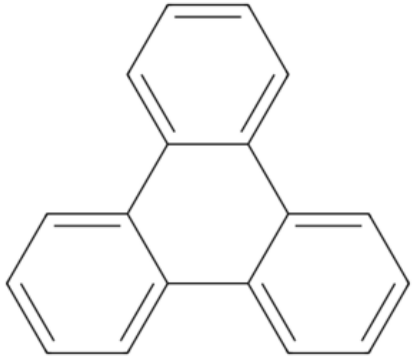

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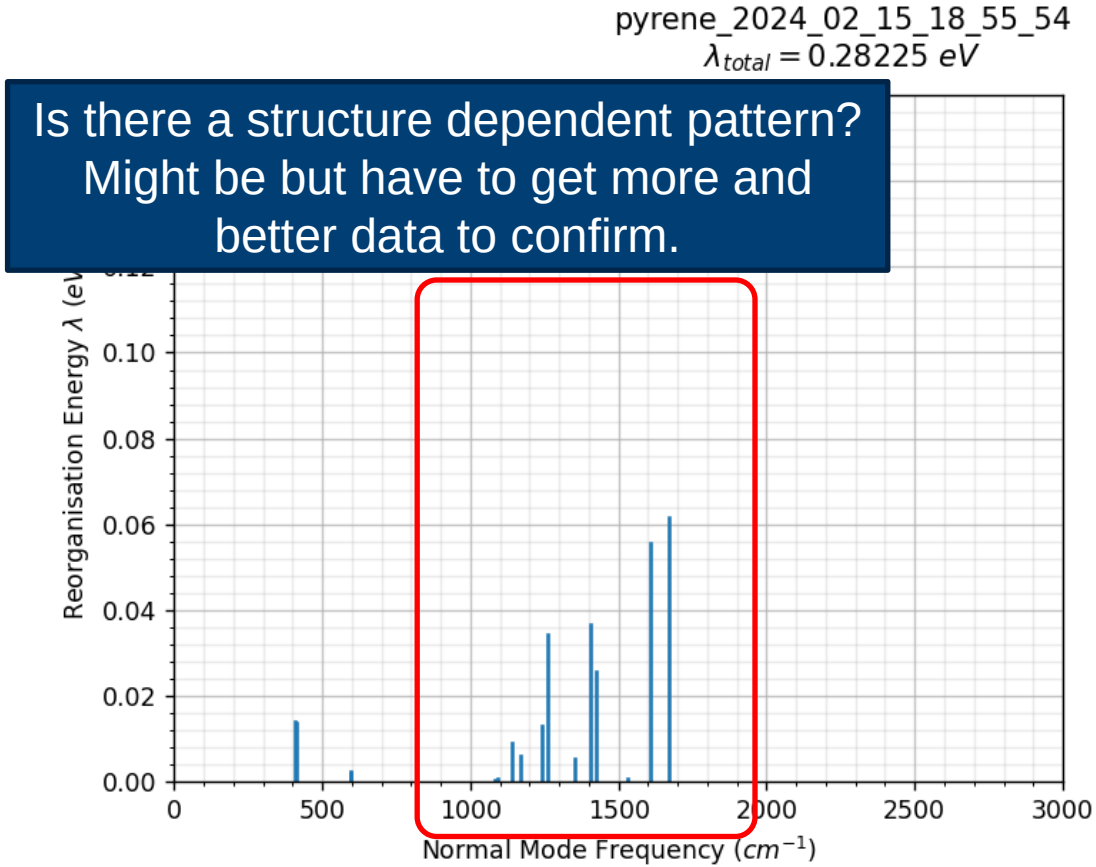

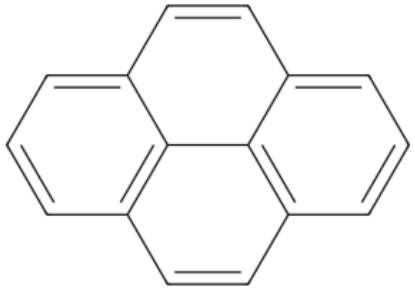

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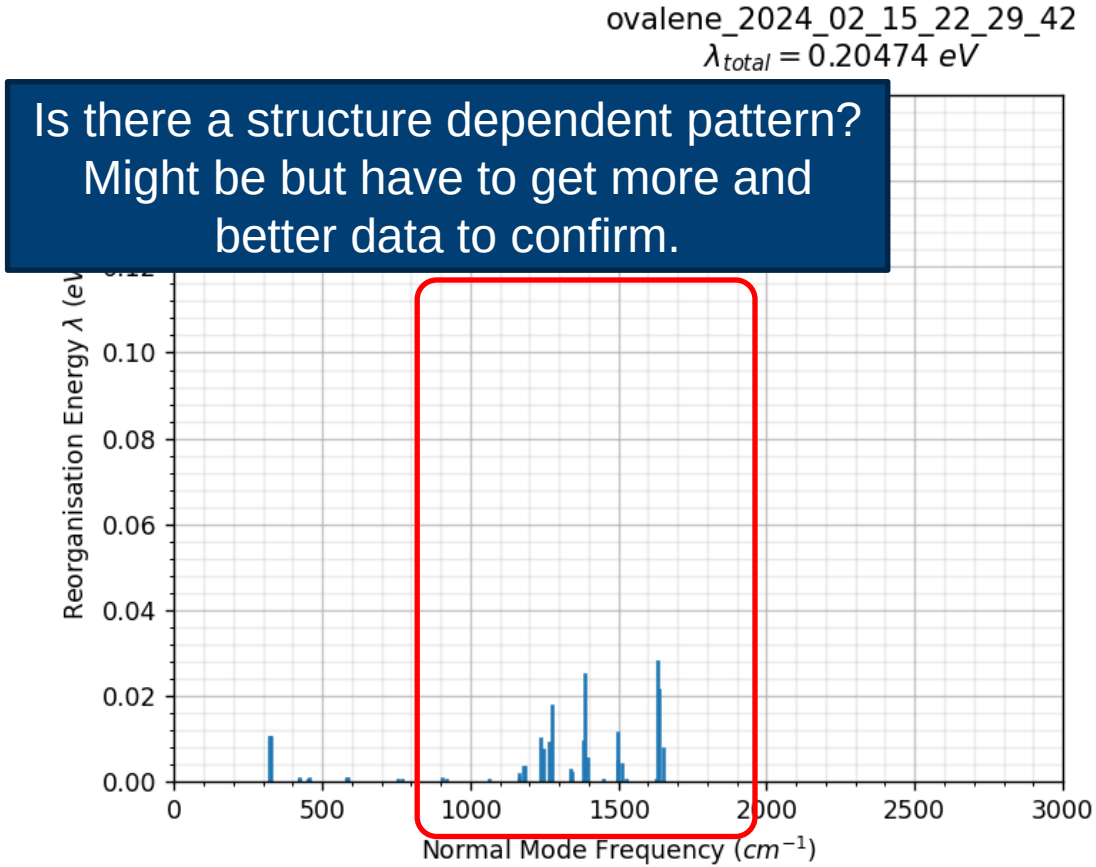
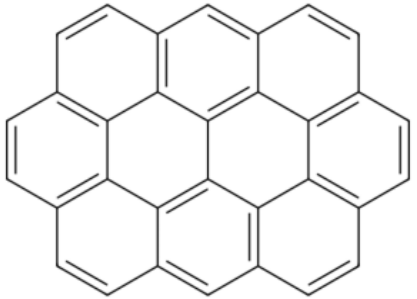
Preview of results:



Is there a structure dependent pattern? Might be but have to get more and better data to confirm.



Speed Run

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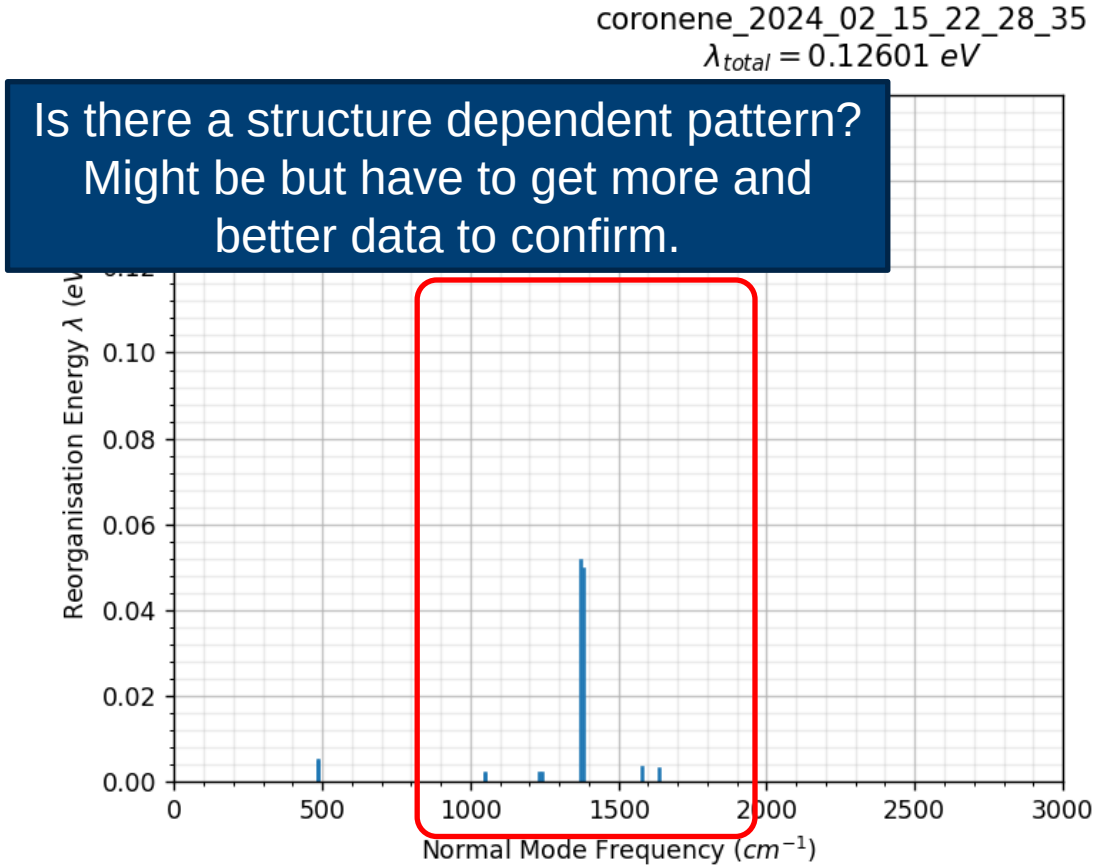
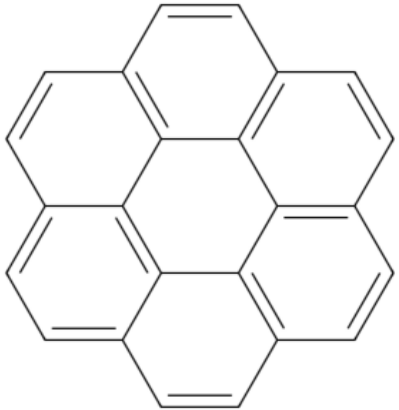
Preview of results:





Speed Run

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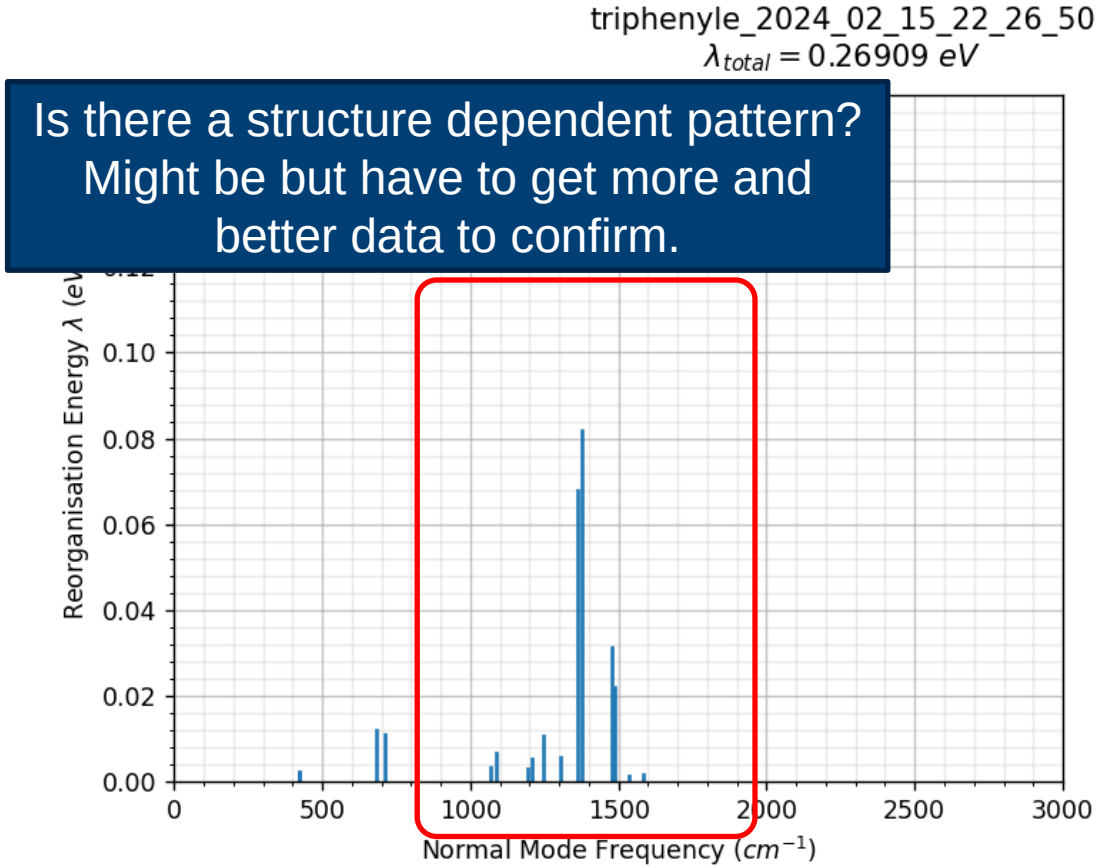
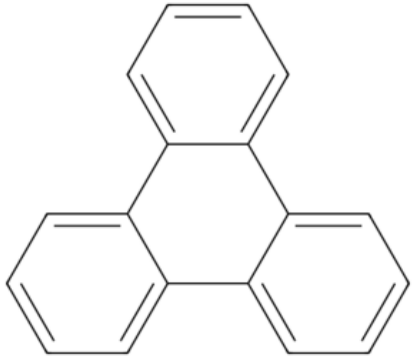
Preview of results:





Speed Run

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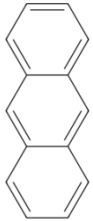
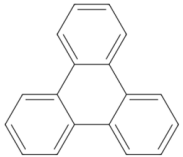
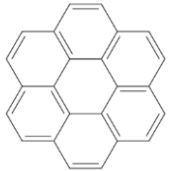
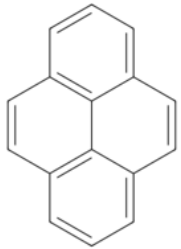
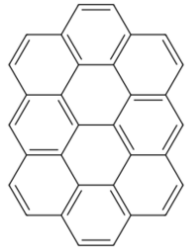
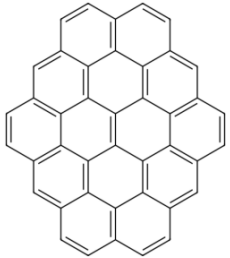
Preview of results: Symmetry?

	Benzene	Anthracene	Triphenylene	Coronene	Pyrene	Ovalene	Tetradeca-cyclo
S1	0.257	0.432	0.269	0.126	0.282	0.204	*
C1	0.294	0.139	0.185	*	0.153	0.096	0.068
C-1	0.002*	0.196	0.250	0.170	0.214	0.122	0.144
HL Gap	6.600	3.552	4.839	4.001	3.810	2.916	2.516

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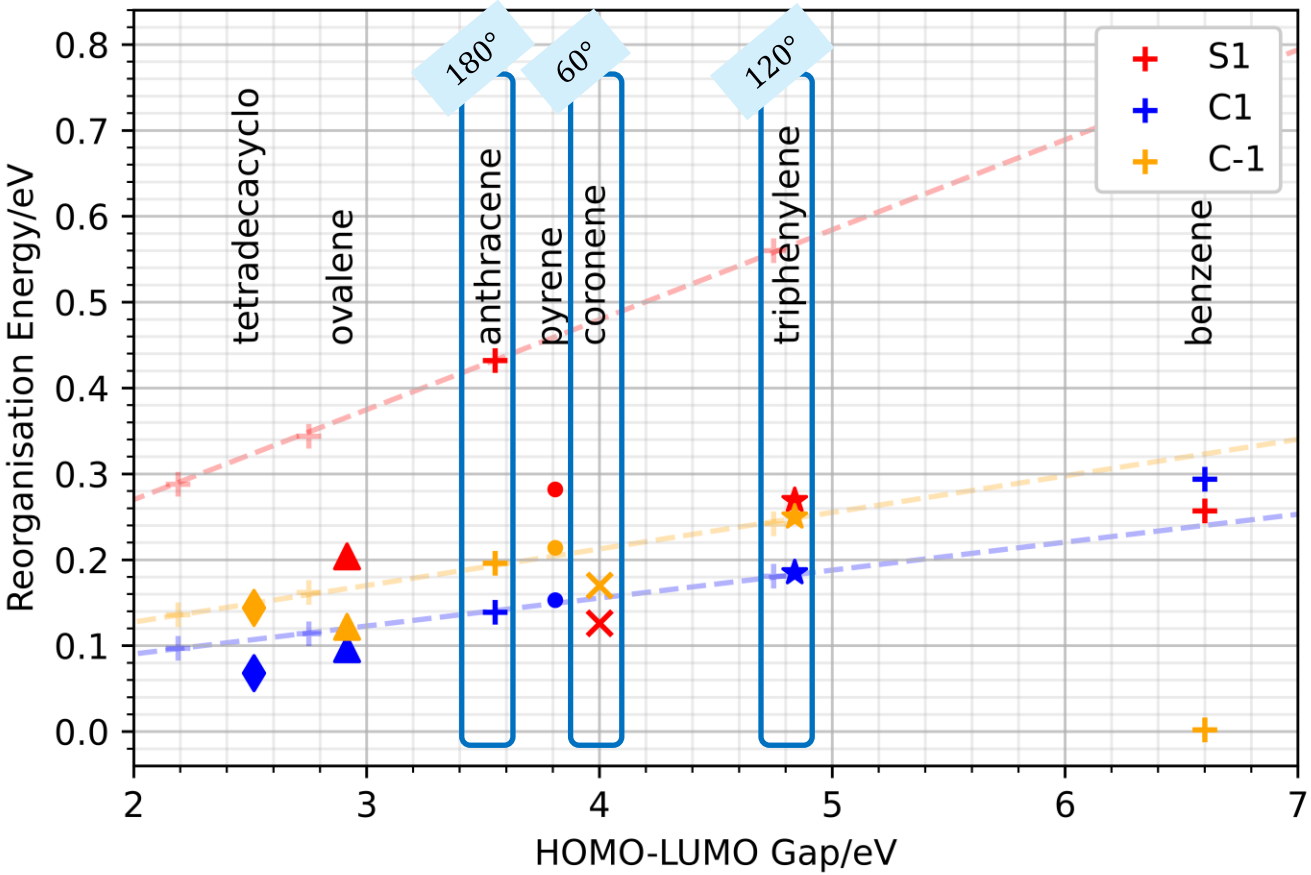
Preview of results: Symmetry?



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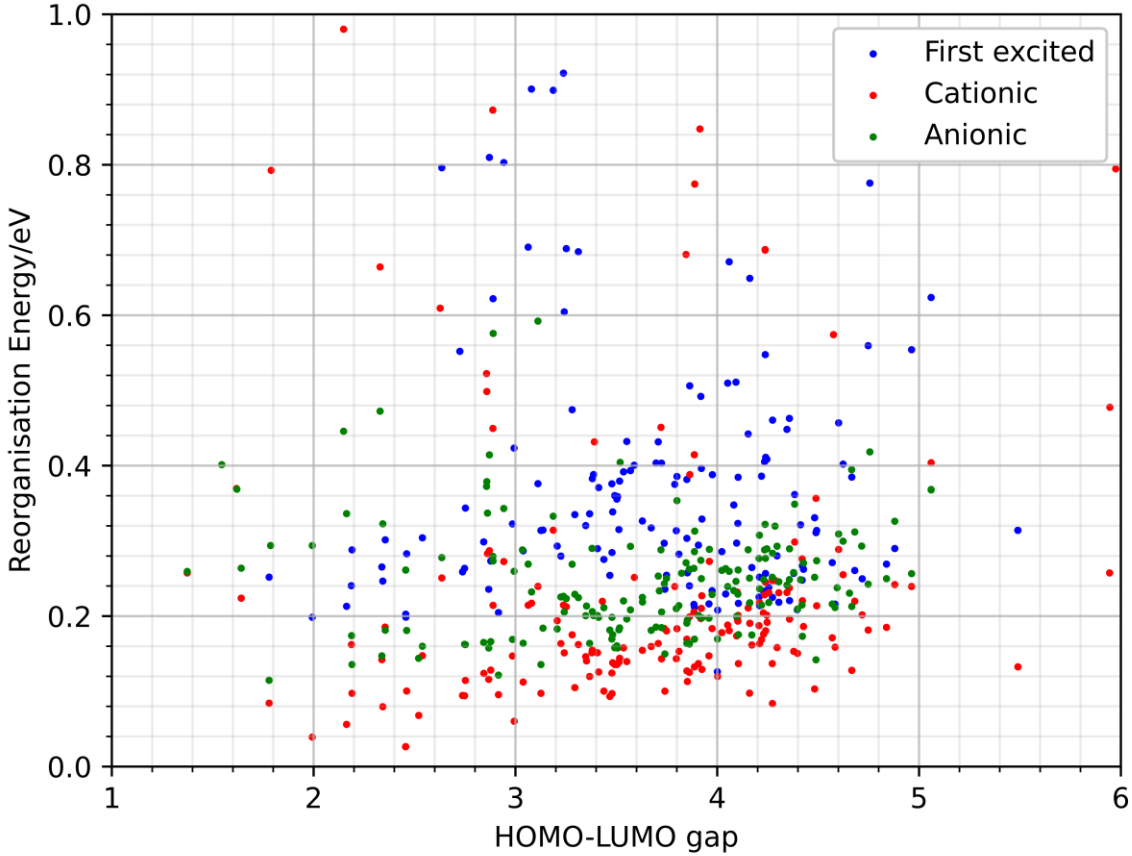
Preview of results: Failed Cases



Left figure: Plot of the reorganisation energies against HOMO-LUMO gap for all the processed molecules, categorised by transition.

Upon inspection, ‘failure’ is likely to be caused by:

- Double sulphurs
- Problems with conjugation
- Molecule bonds breaking during geometry optimisation

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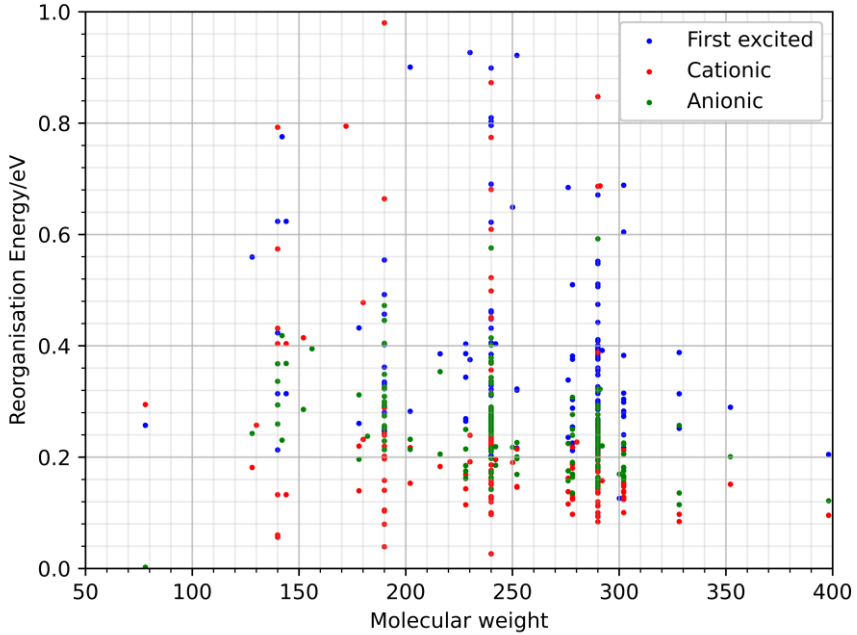
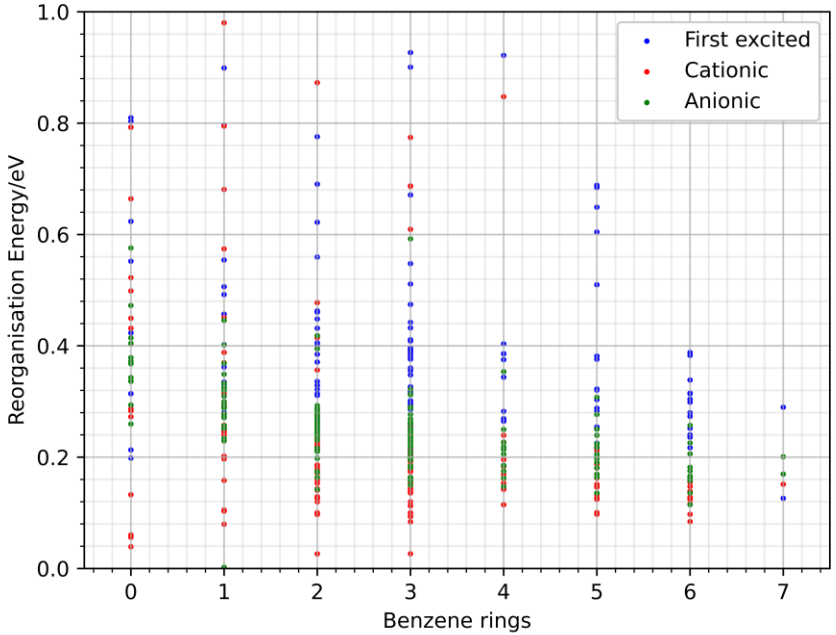
Preview of results: Failed Cases

The ‘noise’ would seriously impact the ability to perform a high-throughput automated analysis of the relationship between molecules and their properties.





What this means: Next Steps

- For linear oligophenes with only complete rings, generally **larger molecules would have smaller reorganisation energies**.
- The **more ‘together’ the molecules are, the lower the reorganisation energy**, although this would require further investigation and a stronger justification.
- To improve data collection and analysis, explore how values are **dependent** on **DFT methods and basis sets**.
- Could also **reduce fail cases** by optimising from smaller to larger basis sets, adjusting the trust radius for Gaussian16 optimisation (maximum step size), and explicitly defining connectivity.
- If better data sets are obtained, could be possible to perform **large scale analysis on electronic properties** and perhaps even predict properties.