# Si
Silico
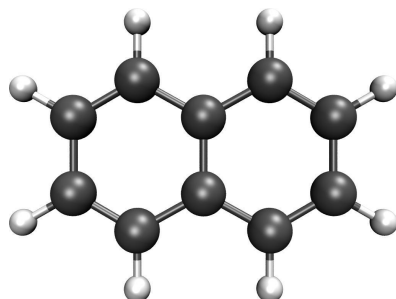
# A Report On The Calculation Of The Optimised Structure And Excited States Of Naphthalene At The MP2/cc-pVDZ Level

osl - 07th June 2022



## Abstract

The calculation of optimised structure and excited states for the system 'Naphthalene' is presented, accompanied by automated analysis and image generation provided by the Silico software package. The calculations were performed using the Turbomole software package(s) at the MP2/cc-pVDZ level of theory. The total self-consistent field (SCF) energy of the system was found to be -10432.31 eV after 7 steps. The total Møller–Plesset (MP) energy of the system was found to be -10467.16 eV after 14 steps. The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) were calculated to be -7.78 and 2.37 eV respectively, corresponding to a HOMO-LUMO band gap of 10.15 eV. The permanent dipole moment (PDM) was calculated to be 0.00 D. In total, 4 excited states were calculated with singlet and triplet multiplicity. The most intense absorption peak was calculated to be at 246 nm. The lowest energy singlet and triplet excited states ($S_1$ and $T_1$) were calculated to be 4.37 and 3.27 eV (284 and 379 nm) respectively, corresponding to a singlet/triplet splitting energy ($\Delta E_{ST}$) of 1.10 eV.

***Table 1:*** *Summary of overall calculation metadata. [a]: The date and time at which the calculation was completed. [b]: Total combined duration in real-time (wall-time) for all components of the calculation. [c]: Temperature used for thermochemistry analysis. [b]: Pressure used for thermochemistry analysis.*

| Calculation no. | Date[a] | Duration[b] | Success (Converged) | Computational package | Level of theory | Calculations | Wavefunction | Multiplicity | T[c] / K | p[d] / atm |
|---|---|---|---|---|---|---|---|---|---|---|
| Combined | 07/06/2022 18:50:12 | 13 m, 5 s | True (True) | Turbomole (7.5.0) | MP2/cc-pVDZ | Optimisation, Excited States | restricted | 1 (singlet) | N/A | N/A |
| 1 | 07/06/2022 18:31:50 | 4 m, 57 s | True (True) | Turbomole (7.5.0) | MP2/cc-pVDZ | Optimisation | restricted | 1 (singlet) | N/A | N/A |
| 2 | 07/06/2022 18:40:35 | 4 m, 2 s | True (N/A) | Turbomole (7.5.0) | MP2/cc-pVDZ | Excited States | restricted | 1 (singlet) | N/A | N/A |
| 3 | 07/06/2022 18:50:12 | 4 m, 5 s | True (N/A) | Turbomole (7.5.0) | MP2/cc-pVDZ | Excited States | restricted | 1 (singlet) | N/A | N/A |

## Summary Of Results

### Scf Energy

***Table 2:*** *Summary of SCF energy properties.*

| | |
|---|---|
| **No. of steps** | 7 |
| **Final energy** | -10432.3114 eV |
| **Final energy** | -1,006,565 kJ·mol$^{-1}$ |

### Mp Energy

***Table 3:*** *Summary of MP energy properties.*

| | |
|---|---|
| **No. of steps** | 14 |
| **Final energy** | -10467.1582 eV |
| **Final energy** | -1,009,927 kJ·mol$^{-1}$ |

### Geometry

***Table 4:*** *Summary of geometry properties.*

| | |
|---|---|
| **Formula** | $C_{10}H_8$ |
| **Molar mass** | 128.1705 g·mol$^{-1}$ |
| **Alignment method** | Minimal |
| **X extension** | 6.80 Å |
| **Y extension** | 5.02 Å |
| **Z extension** | 0.00 Å |
| **Linearity ratio** | 0.26 |
| **Planarity ratio** | 1.00 |

### Molecular Orbitals

***Table 5:*** *Summary of HOMO & LUMO properties.*

| | |
|---|---|
| $E_{HOMO,LUMO}$ | 10.15 eV |
| $E_{HOMO}$ | -7.78 eV |
| $E_{LUMO}$ | 2.37 eV |

### Permanent Dipole Moment

***Table 6:*** *Summary of the permanent dipole moment properties.*

| | |
|---|---|
| **Total** | < 0.01 D |
| **X axis angle** | 90.00 ° |
| **XY plane angle** | 84.81 ° |

### Excited States

***Table 7:*** *Summary of the calculated excited states. $E_x$: The energy of excited state x. $\lambda_x$: The wavelength of a photon of equivalent energy to excited state x. $f_x$: The oscillator strength of the excited state transition x. $\Delta E_{xy}$: The difference in energy between the lowest excited states of multiplicity x and y.*

| | |
|---|---|
| **No. calculated singlets** | 2 |
| $E_{S_1}$ | 4.37 eV |
| $\lambda_{S_1}$ **(colour, CIE)** | 284 nm (Ultraviolet ■, (0.00, 0.00)) |
| $f_{S_1}$ | < 0.01 |
| **No. calculated triplets** | 2 |

| | |
|---|---|
| $E_{T_1}$ | 3.27 eV |
| $\lambda_{T_1}$ **(colour, CIE)** | 379 nm (Ultraviolet ■, (0.17, 0.00)) |
| $f_{T_1}$ | 0.00 |
| $\Delta E_{ST}$ | 1.10 eV |
| **Simulated Absorption Peaks** | 246 nm |

## Methodology

### Metadata

This report was generated from the combined results of three individual calculations. The individual metadatas for each separate calculation are presented in the following sections, and the overall calculation was performed using the **Turbomole (7.5.0)** program, the **HF and MP2** methods and the **cc-pVDZ** basis set. It was completed on the **07th June 2022** after a total duration of **13 m, 5 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals. The full calculation metadata is tabulated in table 1.

The calculation of the optimised structure was performed using the **Turbomole (7.5.0)** program, the **HF and MP2** methods and the **cc-pVDZ** basis set. It was completed on the **07th June 2022** after a total duration of **4 m, 57 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

The calculation of the excited states was performed using the **Turbomole (7.5.0)** program, the **HF and MP2** methods and the **cc-pVDZ** basis set. It was completed on the **07th June 2022** after a total duration of **4 m, 2 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

The calculation of the excited states was performed using the **Turbomole (7.5.0)** program, the **HF and MP2** methods and the **cc-pVDZ** basis set. It was completed on the **07th June 2022** after a total duration of **4 m, 5 s** and **finished successfully**. The base multiplicity of the system under study was **1 (singlet)**. Finally, a **restricted wavefunction** was used, resulting in a single set of doubly occupied orbitals.

### Analysis

The report presented here was generated using the Silico software package. This toolset relies upon a number of third-party applications and libraries which should be cited appropriately in derivative works. In particular, the calculation results described within were parsed by the cclib library.[1] Scientific constants which were used, among other things, for the interconversion of scientific units were provided by SciPy.[2] Commission internationale de l'éclairage (CIE) coordinates, along with visual representations of the equivalent colour, were calculated using the Colour Science library.[3] Three-dimensional plots of atom positions and calculated densities, including molecular orbitals, were rendered using Visual Molecular Dynamics (VMD)[4] and the Tachyon ray-tracer.[5] Finally, two-dimensional graphs were plotted using the MatPlotlib library,[6] while this report itself was prepared using the Mako template library[7] and the Weasyprint library[8], the latter of which was responsible for generation of the PDF file.

## Discussion

### Total SCF Energy

The total energy of the system was calculated at the **self-consistent field (SCF)** level, corresponding to the energy calculated by the Hartree-Fock (HF) method, over a total of seven steps, the results of which are displayed in figure 1. The energy calculated by the final step was -10432.31 eV, corresponding to -1,006,565 KJmol⁻¹. A plot of the total SCF electron density is shown in figure 2.
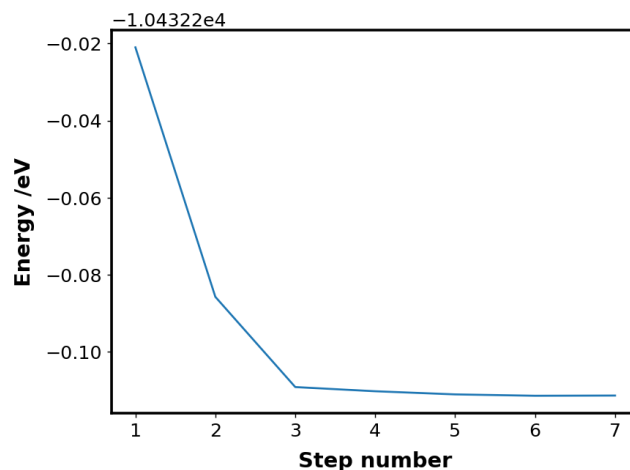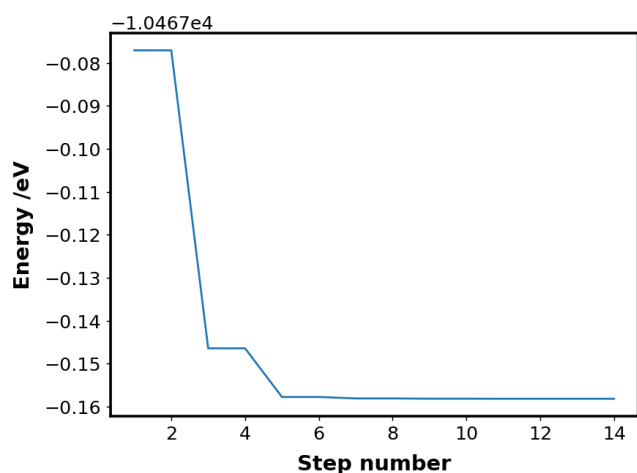


***Figure 1:*** *Graph of calculated energies at the self-consistent field (SCF) level.*
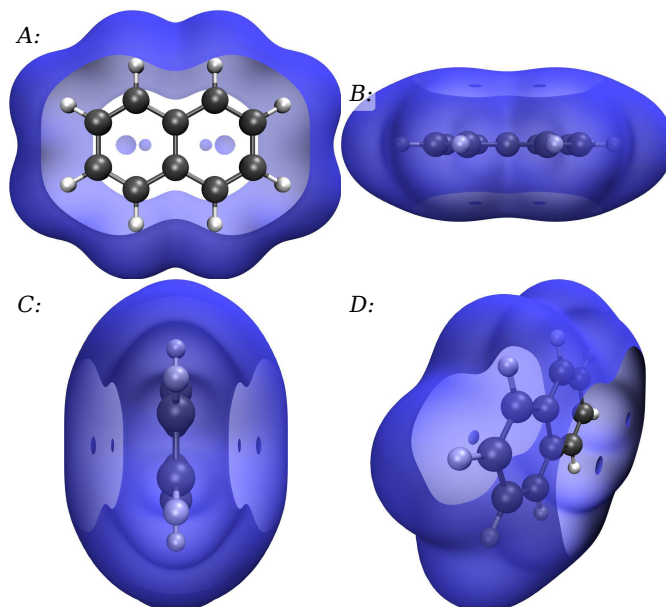


***Figure 2:*** *Plot of the total SCF electron density, plotted with an isovalue of 0.0004. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

### Total MP Energy

The total energy of the system was calculated at the **Møller–Plesset (MP)** level over a total of 14 steps, the results of which are displayed in figure 3. The energy calculated by the final step was -10467.16 eV, corresponding to -1,009,927 KJmol⁻¹.

***Figure 3:*** *Graph of calculated energies at the Møller–Plesset (MP) level.*

## Geometry

The **empirical formula** of the studied system was $C_{10}H_8$, corresponding to a **molecular mass** of 128.17 gmol$^{-1}$. The molecular geometry was aligned to the cartesian (X, Y and Z) axes by the **Minimal (MIN)** method. Using this method, the **extent of the molecular system** in the X, Y and Z axes ($L_X$, $L_Y$ and $L_Z$, corresponding to the molecular width, length and height respectively) was determined to be 6.80, 5.02 and 0.00 Å respectively. These extensions give rise to a **molecular linearity ratio** ($1-(L_Y/L_X)$) and **planarity ratio** ($1-(L_X/L_Y)$) of 0.26 and 1.00 respectively.

## Permanent Dipole Moment

The calculated **permanent dipole moment** was < 0.01 D, with a vector (x,y,z) of 0.00, 0.00, 0.00 D. The angle between the dipole moment vector and the x-axis was 90.00 °, while the angle between the dipole moment and the xy-plane was 84.81 °. A plot of the permanent dipole moment is shown in figure 4.
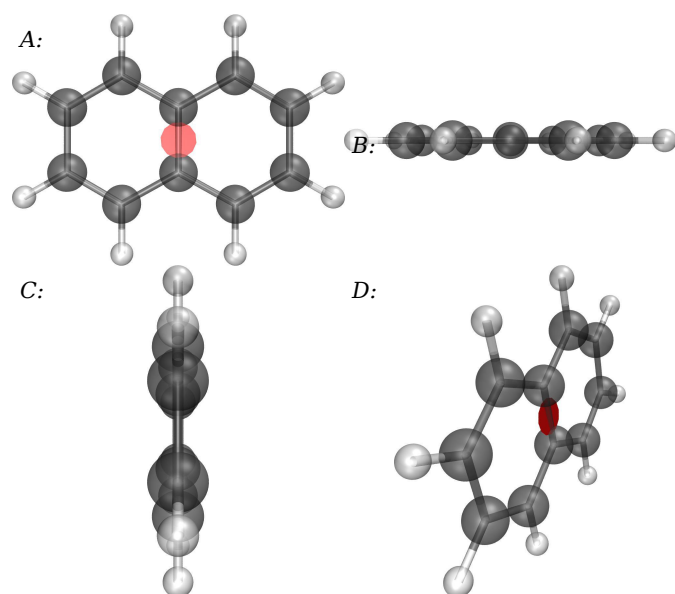


***Figure 4:*** *The permanent dipole moment (red arrow) plotted against the aligned molecular geometry with a scale of 1 Å = 1.0 D. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

## Molecular Orbitals

In total, 180 doubly occupied molecular orbitals were calculated, divided into 34 occupied orbitals and 146 unoccupied (or virtual)

orbitals. The calculated energies of the **HOMO and LUMO** were -7.78 and 2.37 eV respectively, corresponding to a **HOMO-LUMO band gap** of 10.15 eV (figure 10). Plots of the orbital density for the HOMO-1, HOMO, LUMO and LUMO+1 are shown in figures 5-7 and 9 respectively, while the orbital overlap between the HOMO and LUMO is shown in figure 8.
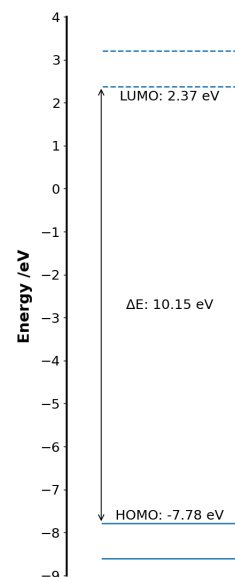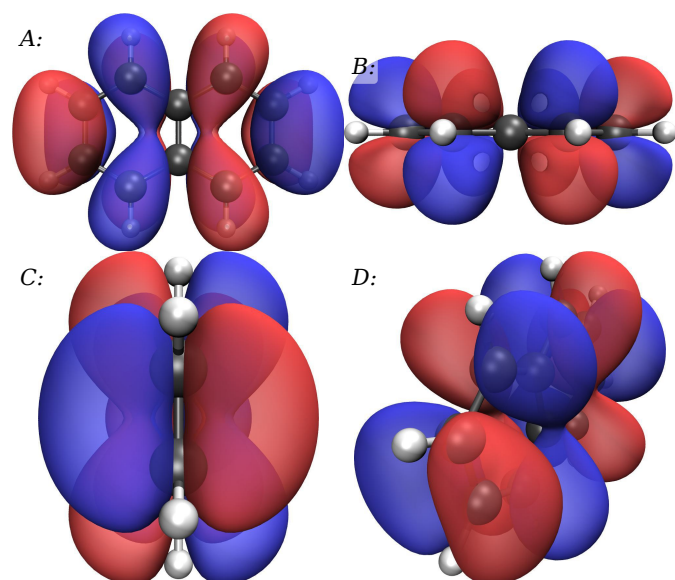


***Figure 10:*** *Graph of the calculated molecular orbital energies in close proximity to the HOMO-LUMO gap. Solid lines: occupied orbitals, dashed lines: virtual orbitals.*
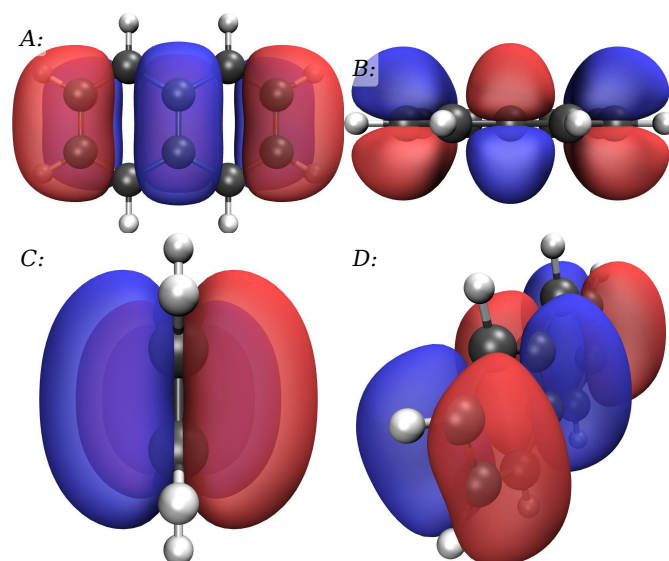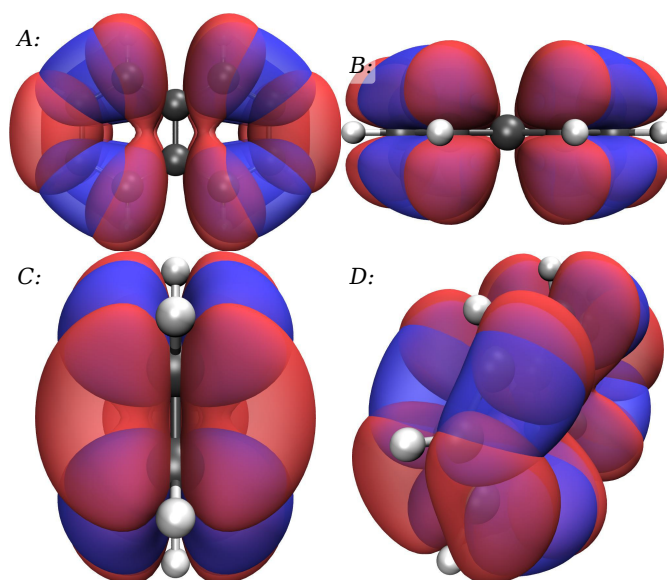


***Figure 5:*** *Orbital density plots of the HOMO-1, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*
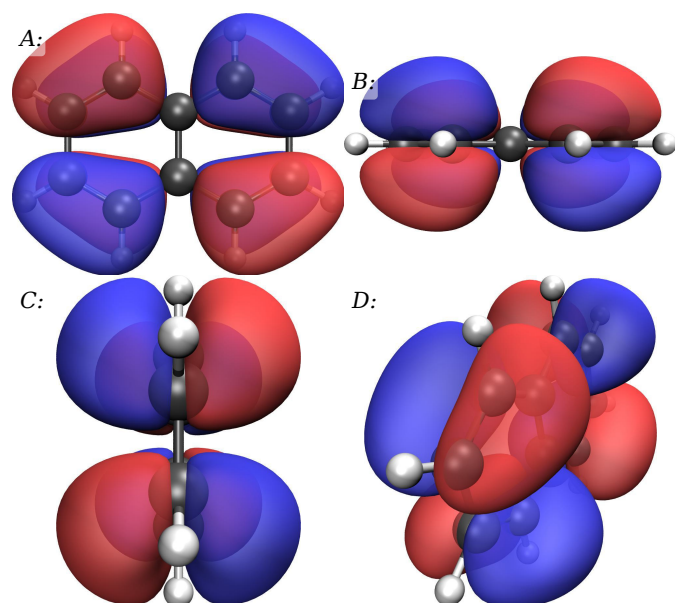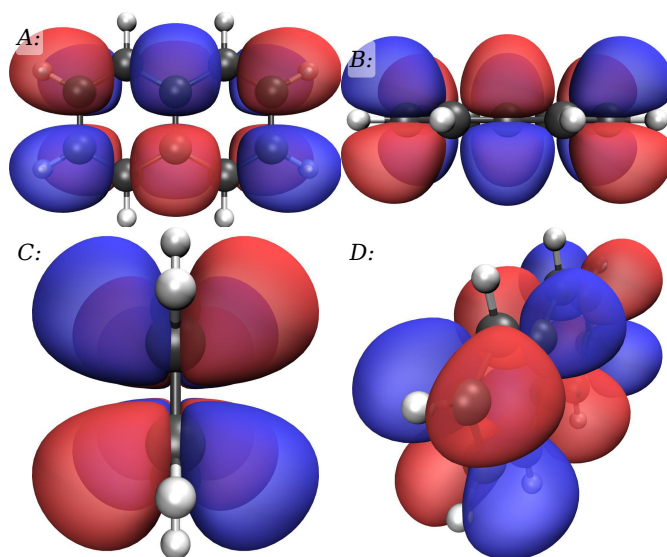
**Figure 6:** *Orbital density plots of the HOMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*



**Figure 8:** *Orbital density plots of the HOMO (blue) and LUMO (red), plotted simultaneously with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*
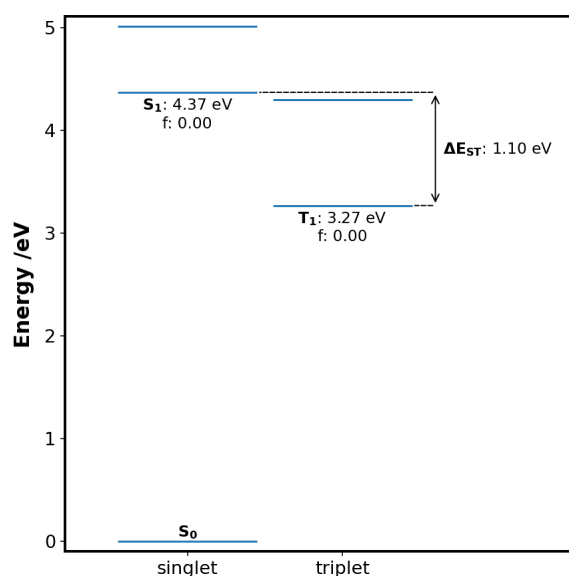


**Figure 7:** *Orbital density plots of the LUMO, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*



**Figure 9:** *Orbital density plots of the LUMO+1, plotted with isovalue: 0.02. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*
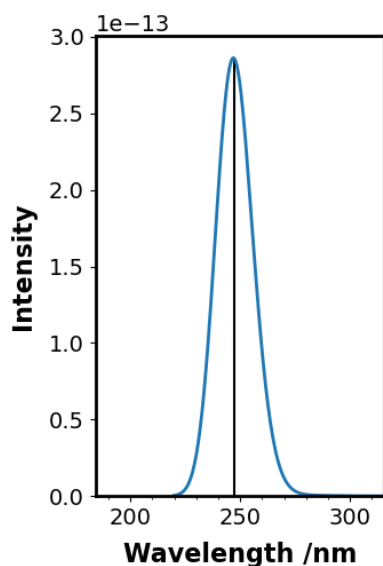
## Excited States

In total, the energies of four electronic excited states were calculated (figure 11), consisting of two states with a multiplicity of singlet and two of multiplicity triplet. The energy of the lowest **singlet excited state ($S_1$)** was 4.37 eV, corresponding to absorption by a photon with a wavelength of 284 nm, an ultraviolet 'color' ■ and CIE coordinates of (0.00, 0.00), while the energy of the **$T_1$** was 3.27 eV (379 nm, ultraviolet ■, CIE: (0.17, 0.00)). The difference in energy between the $S_1$ and $T_1$ excited states **($\Delta E_{ST}$)** was therefore 1.10 eV. A complete table of the calculated excited state properties is available in table 8. In addition, an electronic transition spectrum was simulated using a gaussian function with full-width at half maximum (FWHM) of 0.40 eV, from which the **one most intense peak** was found at 246 nm. The full simulated absorption spectrum is shown in figure 12. Finally, the **difference in density** between each excited state and the ground was calculated and is shown in figures 13-16.
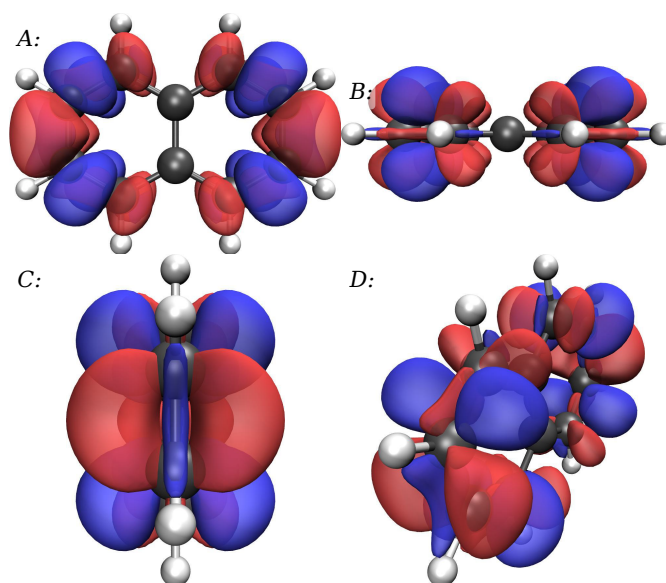
**Figure 11:** *Graph of the calculated excited states. f: oscillator strength of the relevant ground to excited state transition.*



**Figure 12:** *Graph of the simulated absorption spectrum. Excited states are shown as vertical black lines, while peaks simulated with a gaussian function with FWHM: 0.40 eV are shown as a blue line. Peaks can be found at: 246 nm.*



**Figure 13:** *Difference density plot of the hole (blue) & electron (red) of the $T_1$ state, plotted with isovalue: 0.001. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*
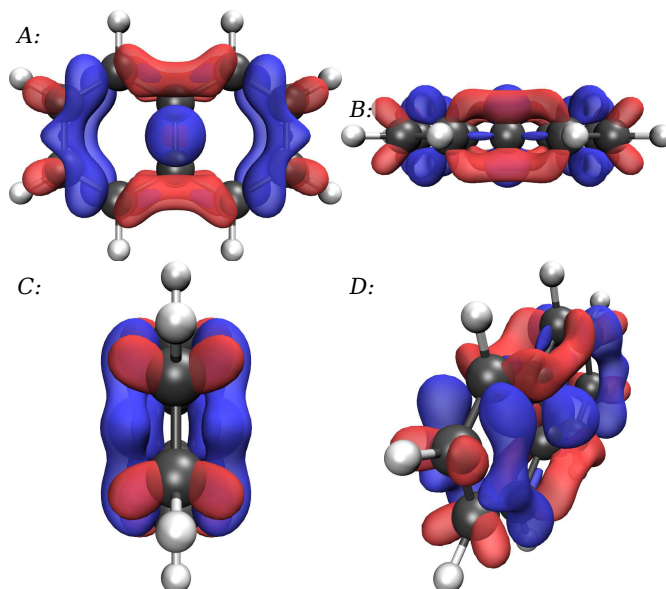


**Figure 14:** *Difference density plot of the hole (blue) & electron (red) of the $T_2$ state, plotted with isovalue: 0.001. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

A:

B:

C:

D:
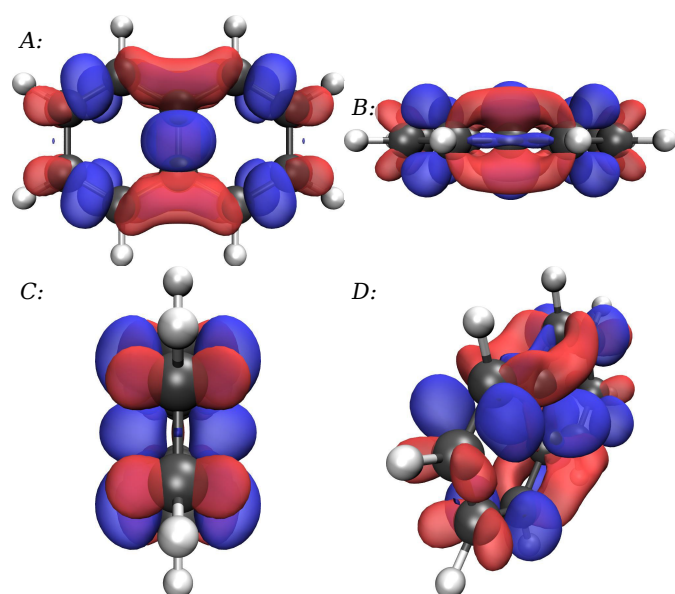
**Figure 15:** *Difference density plot of the hole (blue) & electron (red) of the $S_1$ state, plotted with isovalue: 0.001. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*
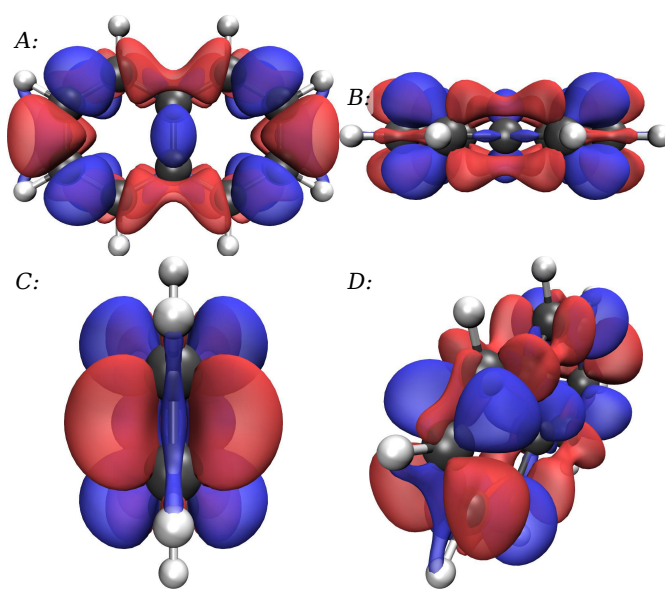
A:

B:

C:

D:

**Figure 16:** *Difference density plot of the hole (blue) & electron (red) of the $S_2$ state, plotted with isovalue: 0.001. A: In the X/Y plane, B: In the X/Z plane, C: In the Z/Y plane, D: 45° to the axes.*

# Tables Of Results

## Atom Coordinates

**Table 9:** *Coordinates of the atoms of the system under study, as aligned to the cartesian axes by the Minimal method.*

| Element | X Coord /Å | Y Coord /Å | Z Coord /Å |
|---|---|---|---|
| C | -1.2509141 | -1.4118092 | -0.0000069 |
| C | -2.4487537 | -0.7132682 | 0.0000087 |
| C | -2.4487547 | 0.7132694 | 0.0000104 |
| C | -1.2509134 | 1.4118084 | -0.0000068 |
| C | -0.0000000 | 0.7179339 | -0.0000210 |
| C | -0.0000000 | -0.7179354 | -0.0000202 |
| C | 1.2509141 | -1.4118092 | -0.0000071 |
| C | 1.2509134 | 1.4118084 | -0.0000084 |
| C | 2.4487547 | 0.7132694 | 0.0000099 |
| C | 2.4487537 | -0.7132682 | 0.0000093 |
| H | -1.2480933 | -2.5080746 | -0.0000131 |
| H | -3.4000079 | -1.2561870 | 0.0000192 |
| H | -3.4000083 | 1.2561881 | 0.0000264 |
| H | -1.2480915 | 2.5080739 | -0.0000147 |
| H | 1.2480933 | -2.5080746 | -0.0000148 |
| H | 1.2480915 | 2.5080739 | -0.0000190 |
| H | 3.4000083 | 1.2561881 | 0.0000266 |
| H | 3.4000079 | -1.2561870 | 0.0000218 |

## Molecular Orbitals

**Table 10:** *Energies of the calculated molecular orbitals.*

| Level | Label | Symmetry | Energy /eV |
|---|---|---|---|
| 50 | LUMO+15 | A | 11.9600 |
| 49 | LUMO+14 | A | 11.7352 |
| 48 | LUMO+13 | A | 10.6261 |
| 47 | LUMO+12 | A | 10.4351 |
| 46 | LUMO+11 | A | 7.9455 |
| 45 | LUMO+10 | A | 7.4055 |
| 44 | LUMO+9 | A | 7.3699 |
| 43 | LUMO+8 | A | 6.8297 |
| 42 | LUMO+7 | A | 6.4869 |
| 41 | LUMO+6 | A | 6.3480 |
| 40 | LUMO+5 | A | 5.4144 |
| 39 | LUMO+4 | A | 5.4053 |
| 38 | LUMO+3 | A | 4.9896 |
| 37 | LUMO+2 | A | 4.7431 |
| 36 | LUMO+1 | A | 3.2023 |
| 35 | **LUMO** | **A** | **2.3705** |
| 34 | **HOMO** | **A** | **-7.7835** |
| 33 | HOMO-1 | A | -8.6036 |
| 32 | HOMO-2 | A | -10.3698 |
| 31 | HOMO-3 | A | -12.0540 |
| 30 | HOMO-4 | A | -12.9253 |
| 29 | HOMO-5 | A | -13.1917 |
| 28 | HOMO-6 | A | -14.1706 |
| 27 | HOMO-7 | A | -14.3301 |
| 26 | HOMO-8 | A | -15.2492 |
| 25 | HOMO-9 | A | -15.7421 |
| 24 | HOMO-10 | A | -15.7464 |
| 23 | HOMO-11 | A | -16.4964 |
| 22 | HOMO-12 | A | -16.8786 |
| 21 | HOMO-13 | A | -18.2419 |
| 20 | HOMO-14 | A | -18.8267 |
| 19 | HOMO-15 | A | -19.1551 |

## Excited States

***Table 8:*** *Energies and other properties of the calculated excited states.*

| Number | Symbol | Symmetry | Energy /eV | Wavelength /nm | Colour (CIE x,y) | Oscillator Strength | Transitions (Probability) |
|---|---|---|---|---|---|---|---|
| 1 | $T_1$ | Triplet-A | 3.2689 | 379.29 | Ultraviolet ■ (0.17, 0.00) | 0.0000 | HOMO → LUMO (0.85)<br>HOMO-2 → LUMO+2 (0.06)<br>HOMO-1 → LUMO+1 (0.05) |
| 2 | $T_2$ | Triplet-A | 4.2983 | 288.45 | Ultraviolet ■ (0.00, 0.00) | 0.0000 | HOMO-1 → LUMO (0.49)<br>HOMO → LUMO+1 (0.46)<br>HOMO-3 → LUMO+2 (0.02) |
| 3 | $S_1$ | Singlet-A | 4.3707 | 283.67 | Ultraviolet ■ (0.00, 0.00) | 0.0002 | HOMO-1 → LUMO (0.49)<br>HOMO → LUMO+1 (0.48) |
| 4 | $S_2$ | Singlet-A | 5.0100 | 247.47 | Ultraviolet ■ (0.00, 0.00) | 0.0880 | HOMO → LUMO (0.90)<br>HOMO-1 → LUMO+1 (0.08) |

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**6.** J. D. Hunter, *Computing in Science & Engineering,* 2007, **9,** 90--95

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**8.** K. Community, https://weasyprint.org, (accessed May 2020)