D1CH9116 - MMCO

Molecular Modelling applied to organic chemistry

Practical 5: Simulation of the optical properties of organic molecules – absorption

A/ π-π* transition in para-nitroaniline

1/ Configuration Interaction calculation

Optimize the geometry of the para-nitroaniline molecule by performing a configuration interaction calculation at the PM6 level (CI/PM6) with an active space including the two frontier MOs (HOMO and LUMO). Set to 4 the number of final CI eigenstates to be calculated and printed (keyword CISTATE), and calculate the atomic Mulliken charges and dipole moments for all CI eigenstates by checking the option "charge and dipoles" in AGUI (keyword CIDIP). The keyword section of the data file should read as follows:

```
AM1 C.I.=2 CIDIP CISTATE=4 SINGLET TRUSTE T=AUTO VECTORS
```

Check in the output file:

- The symmetry (σ or π) of the frontier orbitals
- The HOMO-LUMO gap
- The dipole moment of the ground state
- The transition energy, wavelength, transition dipole and oscillator strength between the ground and first singlet excited state
- The CI expansion coefficients of the first excited state
- The dipole moment of the first excited state

2/ Description using a 2-state model

a/ Write down the ground and excited state wavefunctions ($|g\rangle$ and $|e\rangle$) of the para-nitroaniline molecule by using a 2-state model implying a neutral form $|N\rangle$ and a zwitterionic form $|Z\rangle$ as basis functions. These latter are orthonormal:

$$\langle N|Z\rangle = \delta_{NZ}$$

b/ Build the associated Hamiltonian matrix **H** with elements:

$$\langle N|\hat{H}|Z\rangle = -\sqrt{2}t,\ E_N = \langle N|\hat{H}|N\rangle = 0,\ E_Z = \langle Z|\hat{H}|Z\rangle = 2\eta$$

c/ Diagonalize the **H** matrix. Write the energies of the eigenstates and their expansion coefficients in the $\{N,Z\}$ basis as a function of t and η.

d/ Deduce the expression of the excitation energy ΔE_{ge}, as a function of the parameter ρ measuring the charge transfer between D and A in the ground state. Plot the evolution of ΔE_{ge} with respect to ρ (using t=1.0 eV), and comment.

e/ We consider the dipole moments associated to the $\left|N\right\rangle$ and $\left|Z\right\rangle$ forms:

$$\mu_N = \left\langle N\middle|\hat{\mu}\middle|N\right\rangle = 0$$

$$\mu_Z = \left\langle Z\middle|\hat{\mu}\middle|Z\right\rangle = \mu_0$$

Write the expression of the transition dipole moment μ_{ge} along the C_2-symmetry axis between the ground ($\left|g\right\rangle$) and excited state ($\left|e\right\rangle$) as a function of μ_0 and ρ. Plot the evolution of μ_{ge} with respect to ρ (using μ_0=1.0 D), and comment.

f/ Owing to $f_{ge} \propto \Delta E_{ge} \left|\mu_{ge}\right|^2$ deduce the oscillator strength f_{ge} between $\left|g\right\rangle$ and $\left|e\right\rangle$. Plot the evolution of f_{ge} with respect to ρ (using t=1.0 eV and μ_0=1.0 D), and comment.

3/ Extraction of the effective electronic parameters

By performing a mapping between the electronic eigenstates $\left|g\right\rangle$ and $\left|e\right\rangle$ obtained in 2/ and the CI eigenstates calculated in 1/, extract the effective electronic parameters t, η and μ_{ge} for the para-nitroaniline molecule.

B/ Impact of the CI active space on the π-π* transition in para-nitroaniline

1/ SCI within π MOs.

Using the geometry obtained in A, identify the MOs of π symmetry from the LCAO coefficients. Perform a CI calculation at the PM6 level (without relaxing the geometry) including only single excitations (SCI) within the complete set of π orbitals (use the selection tool of AGUI to exclude the σ-orbitals from the active MO space). Check the character of the first allowed excited state (transition energy, oscillator strength and CI expansion coefficients).

2/ Impact of the number of active MOs.

Perform a series SCI/PM6 calculations on π orbitals while reducing progressively the number of MOs included in the CI process. Check in each case:

- the energy of the ground state
- the number of Slater determinants considered in the CI process

- the character of the first allowed excited state (transition energy, oscillator strength and CI expansion coefficients). *Do not consider electronic states with oscillator strength lower than 0.1*.

3/ Impact of high-order excitations.

Using the full π-MO space, perform CI calculations including i) single and double excitations (SDCI) and ii) all high-order excitations (*Full* CI). In ii), check the impact of increasing from 1000 to 8000 the maximum number of Slater determinants considered in the CI process, by using the CIMAX keyword. Comment.

C/ Optical properties and conjugation strength

We consider the conjugated push-pull compound schematized below.

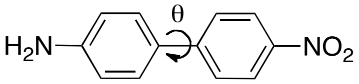

Figure 1: Structure of a push-pull biphenyl derivative

By using the *reaction path* tool of AGUI, run a series of CI calculations at the PM6 level within a minimal HOMO-LUMO active space to investigate the impact of the torsional angle θ on the absorption properties. Comment the results.

D/ Absorption spectra of model push-pull systems

*Reference TD-DFT calculations of the optical properties of oligothiophene derivatives described in sections 1-2 have been reported in [J. Phys. Chem. C **2012**, 116, 11946–11955].*

1/ Impact of the conjugation length

In this section, we aim to investigate the impact of the length of the conjugated bridge on the optical properties of model a push-pull system schematized below (we consider all-*trans* orientations for the thiophene groups). Build several molecular structures by increasing the number n of thiophene rings from 1 to 10, and optimize their geometry at the SCI/PM6 level while imposing the thiophene chain to remain planar (see the optimization procedure described below). The number of (occupied x vacant) MOs included in the SCI calculations will be defined as (5n x 5n) by using the keyword SC.I.=10n, and all Slater determinants will be considered in the CI process (keyword CIMAX=all). Comment the results.

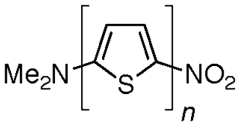

Figure 2: Structure of a model push-pull oligothiophene

Procedure for geometry optimizations:
1 – Optimize the geometrical structure with $n=1$ at the SCI/PM6 level (SC.I.=10), and check the vibrational frequencies to confirm that you obtained a true minimum.
2 – Build the geometrical structure with $n=10$, save the .dat file, and set to zero the optimization flags for all dihedrals.
3 – Create the .dat files for structures with $2 \leq n \leq 9$ from the .dat file generated in step 2.
4 – Run the geometry optimizations for structures with $2 \leq n \leq 10$ (without calculating vibrational frequencies) by using the following keywords:

```
pm6 sc.i.=10 cistate=10n cimax=all singlet truste
```

2/ Impact of the donor and acceptor strengths

In this section, we aim to investigate the impact of the terminal electron-donating and electron-withdrawing groups, using a constant central π-conjugated bridge, namely, a pentathiophene segment. Create the .dat files for the two series of push-pull systems below from the optimized structure with $n=5$ generated in section 1/. Run the geometry optimizations at the SCI(25x25)/PM6 level (keyword SC.I.=50) by using the same constraint as in Step 1 (planarity of the pentathiophene segment), while fully optimizing the geometry of the new donor/acceptor substituent. Comment the results.

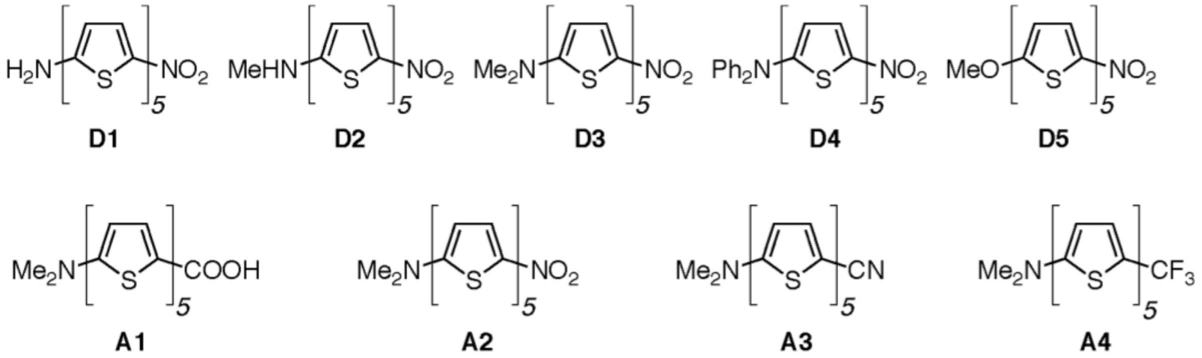

Figure 3: Structure of push-pull pentathiophene derivatives.

3/ A real example: the C212 dye

The most efficient dye-sensitized solar cells (DSCs) actually reported are made of organic-inorganic systems involving a light-harvesting dye molecule anchored onto a mesoporous metal oxide semiconducting film, generally anatase titania (TiO_2), and put into contact with a redox mediator, such as a I^-/I_3^- or Co^{2+}/Co^{3+}-based liquid electrolyte. The C212 dye represented below is prototypical of push-pull molecules used in DSCs.

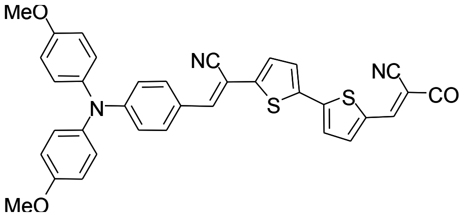

Figure 4: Structure of the C212 dye.

Model the absorption spectrum of the dye at the CI/AM1 level using a (5x5) CI active space and compare to experimental data.

E/ Photochromic systems

We consider below several families of photochromic compounds. Model the absorption spectrum of the two forms at the CI(5x5)/AM1 level. Calculate the displacement of the maximum absorption band along the photochromic reaction.

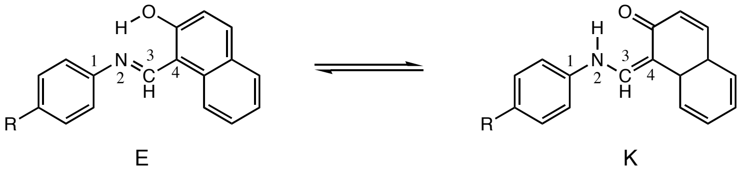

Figure 5: Tautomeric equilibrium of 2-hydroxynaphthaldehyde derivatives

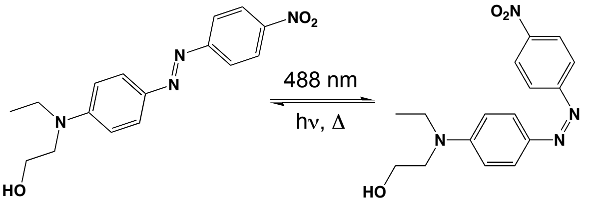

Figure 6: Cis-trans isomerization of Disperse Red 1

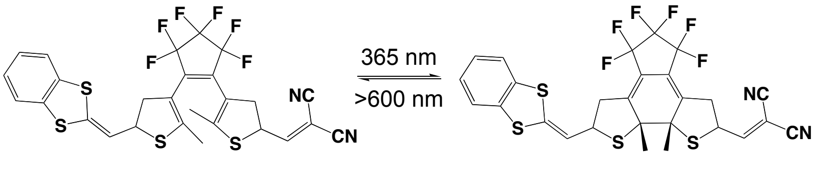

Figure 7: Photochromic equilibrium in a diarylethene derivative