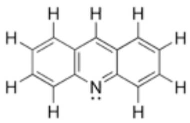
D1CH9116 - MMCO

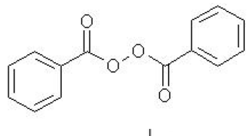
**Molecular Modelling applied to organic chemistry**

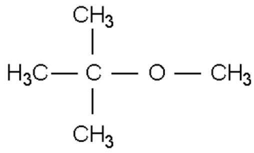
**Practical 1: Structure and electronic properties of organic molecules**

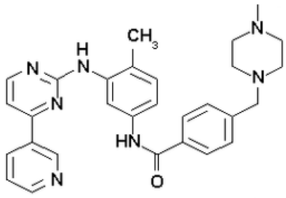
## A/ Handling of the molecular builder

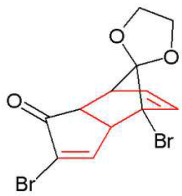
Build the following molecules using the AMPAC Graphical User Interface (AGUI) :











## B/ Structure, electronic and vibrational properties of the water molecule

Optimize the geometry of the water molecule at the AM1 and PM6 levels and check:

- the correct convergence of the calculation (gradient and frequencies)
- the heat of formation
- the relevant structural parameters
- the vibrational frequencies
- the molecular orbitals and their symmetry
- the ionization potential
- the atomic charges
- the orientation and magnitude of the dipole moment

Compare the theoretical results to experiments when available, and comment.

## C/ Impact of the semi-empirical parameterization on the molecular geometry: Example of the N-Acetyl Proline Amide

Reference *ab initio* RHF/6-31G(d,p) calculations have provided the following structural features for the N-Acetyl Proline Amide (Figure 1):

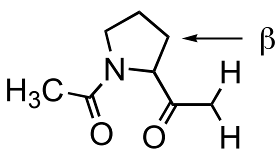



*Figure 1: N-Acetyl Proline Amide.*

- A H-bond of 2.09 Å length exists between one of the H atoms of the amide group and the oxygen of the ether
- The five membered proline ring is in the envelope form, with atoms C-N-C-C approximately in one plane and the β carbon atom out of this plane (N-C-C-$C_b$ = 29°)
- The amide group is planar

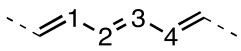
Optimize the geometry of the molecule using the MNDO, AM1, PM3 and PM6 parameterizations, and compare with the reference results.

## D/ Structure and electronic properties of π-conjugated molecules

Optimize the geometry of the increasingly large linear polyenes $C_nH_{2n+2}$ (n=2, 4, 6, 8, 10, 20) at the PM6 level and check:

- the Bond Length Alternation (BLA) along the central part of the molecule
- the shape of the HOMO and LUMO
- the evolution of the HOMO and LUMO energies with n
- the evolution of the HOMO-LUMO gap with n

Plot the BLA and the HOMO-LUMO gap with respect to n, and comment.




$$\boldsymbol{BLA} = \frac{|2d_{23} - d_{12} - d_{34}|}{2}$$

## E/ Structure and electronic properties of push-pull molecules

1/ Optimize the geometry of the acrolein molecule (Fig. 2) at the PM6 level (specify the keywords VECTORS and DENSITY in the field "ADDITIONAL KEYWORDS") and check:

- the relevant structural parameters
- the molecular orbitals
- the atomic charges
- the orientation and magnitude of the dipole moment

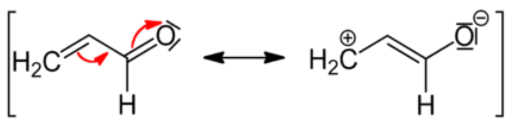



*Figure 2: -M effect of the carbonyl group in the acrolein molecule.*

a/ Write the ground state wavefunction of the acrolein molecule by using a 2-state model implying the neutral form $|N\rangle$ and the zwitterionic form $|Z\rangle$ schematized Fig. 1.

b/ Calculate the π charge on the oxygen atom and evaluate the weights of the neutral and zwitterionic forms in the electronic ground state.

c/ Extract from the density matrix the π bond index between the adjacent atoms, and confirm the contribution of the zwitterionic form in the ground state wavefunction.

d/ Deduce from the shapes of the frontier MOs whether an HOMO-to-LUMO optical excitation would increase or decrease the weight of the zwitterionic form.

2/ Repeat the procedure for the ether molecule shown Figure 2.


*Figure 3: +M effect of the methoxy group in an ether molecule.*

## F/ Photochromic systems

1/ *Cis-trans* isomerization of the Disperse Red 1 (DR1) molecule

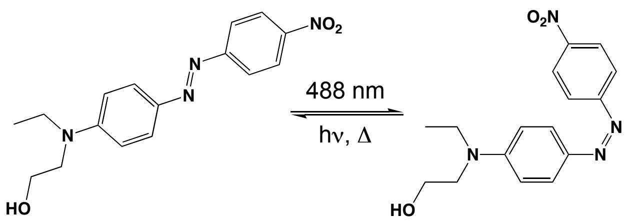



*Figure 4: Cis-trans isomerization of DR1*

a/ Optimize the *cis* and *trans* forms of DR1 at the PM6 level, and check for the two conformers:

- the heat of formation
- the HOMO-LUMO gap

b/ The maximum absorption band of both forms is characterized by a HOMO-to-LUMO electronic transition. What can be expected regarding the displacement of the maximum absorption band along the *trans-cis* commutation?

2/ Answer the same questions for the commutation in the diarylethene system:

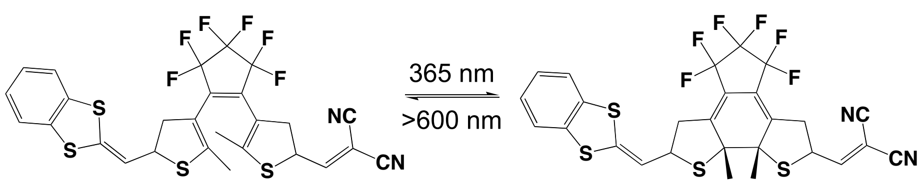



*Figure 5: Photochromic equilibrium in a diarylethene derivative*