D1CH9116 - MMCO

Molecular Modelling applied to organic chemistry

Practical 1: Structure and electronic properties of organic molecules

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.

Results

Property	AM1	PM6	Exp	error wrt exp AM1	error wrt exp PM6
O-H bond (Å)	0,961	0,949	0,957	-0,004	0,008
H-O-H angle (deg)	103,51	107,56	104,5	0,99	-3,06
dipole (D)	1,861	2,068	1,85	-0,011	-0,218
charge O	-0,383	-0,619	/	/	/
charge H	0,191	0,309	/	/	/
Freq, Sym (cm-1)	3585	2613	3943	358	1330
Freq, Asym (cm-1)	3505	2526	3832	327	1306
Freq, Bending (cm-1)	1885	1335	1649	-236	314
IP (eV)	12,464	11,906	12,62	0,156	0,714
Heat of formation (kcal/mol)	-59,24	-54,31	-57,8	1,44	-3,49

Conclusions

AM1 compares better to experiments than PM6 regarding the electronic and strciural properties of the water molecules. As a genral remark, the computed properties always depend on the theoretical level of approximation.

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):

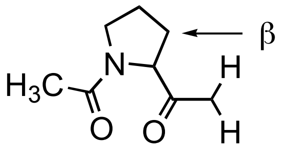
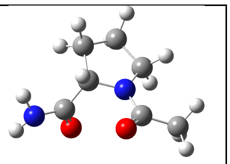
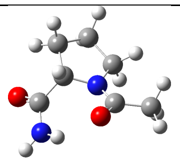
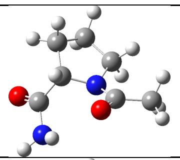
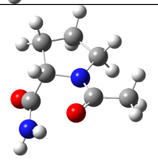


Figure 1: N-Acetyl Proline Amide.

- 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.

Results

MNDO No H bond N-C-C-C_b = -1° Non-planar amide group	
AM1 H bond = 2.14 Å N-C-C-C_b = 1° Planar amide group	
PM3 H bond = 2.59 Å N-C-C-C_b = 0° Non-planar amide group	
PM6 H bond = 2.01 Å N-C-C-C_b = 11° Planar amide group	

Conclusions

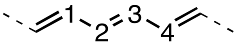
Due to an overestimation of the repulsion between nuclei at large distances, the MNDO parameterization does not predict the existence of H-bonds. Moreover, the proline ring is found planar and the amide group is pyramidal. AM1 predicts the hydrogen bond with the correct geometry and a planar amide group. However, it does not correct the wrong geometry of the proline ring. With PM3, the H-bond is much too long and both the proline ring and amide group geometries are poorly described. PM6 gives the better results with respect to the reference *ab initio* calculations, despite the torsional angle of the proline ring is underestimated (11° vs. 29° at the RHF/6-31G(d) level).

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.

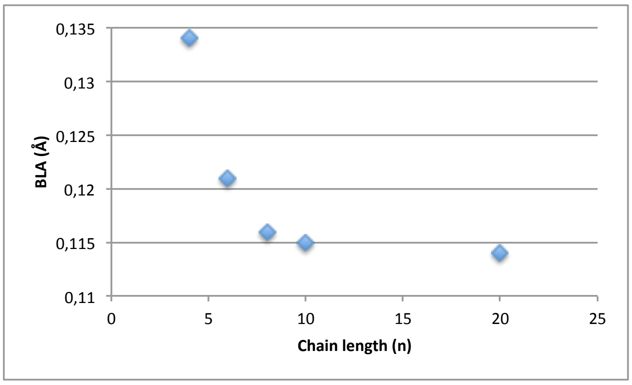


$$BLA = \frac{|2d_{23} - d_{12} - d_{34}|}{2}$$

Results

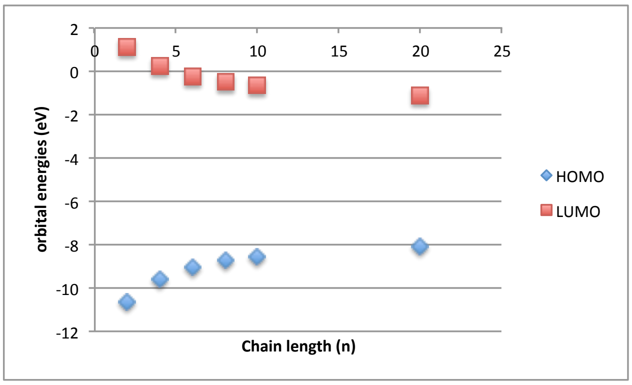
Bond Length Alternation

n	**d_{2-3}**	**$d_{1-2} = d_{3-4}$**	**BLA**
4	1,469	1,335	0,134
6	1,344	1,465	0,121
8	1,461	1,345	0,116
10	1,346	1,461	0,115
20	1,46	1,346	0,114

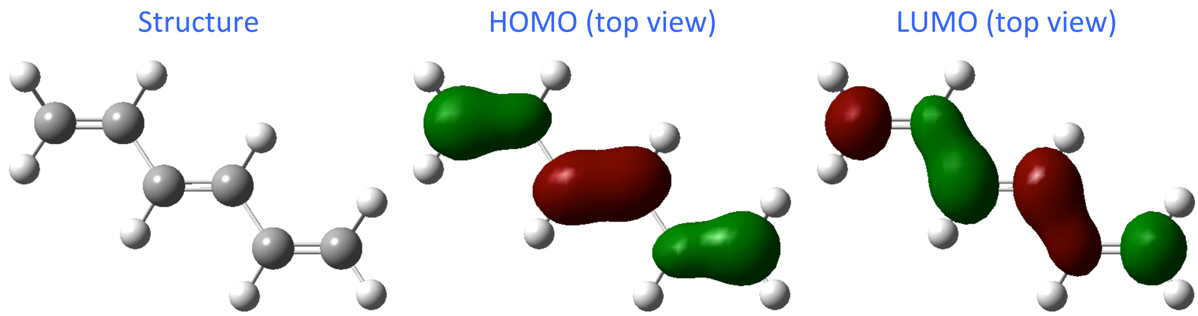


Energies of the frontier orbitals and HOMO-LUMO gap

n	HOMO	LUMO	GAP
2	-10,675693	1,15893	11,834624
4	-9,579752	0,25356	9,833314
6	-9,037731	-0,21602	8,821711
8	-8,72875	-0,49008	8,238665
10	-8,536289	-0,66438	11,834624
20	-8,072675	-1,10879	6,963887



Shape of the frontier orbitals (example for n=6)



HOMOs have nodes on the single bonds. LUMOs have nodes on the double bonds.

Conclusions

When several atomic π-orbitals are combined along a sequence of adjacent atoms in sp^2-hybridisation, a so-called π-conjugated system is formed in which the electrons are delocalised over the atoms of the molecule. The molecular energy levels are affected by π-conjugation: the larger the extent of conjugation, the smaller the energy gap between the frontier orbitals. The reduction of the gap with Increasing n is induced by a reduction of the BLA. This structural parameter is thus an indicator of the extent of the electron conjugation along the molecule.

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

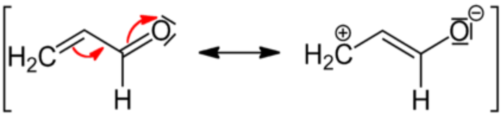


Figure 2: -M effect of the carbonyl group in the acrolein molecule.

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. 2.

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 adjacent atoms, and confirm the contribution of the zwitterionic form in the ground state wavefunction.

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

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

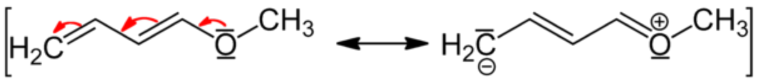


Figure 3: +M effect of the methoxy group in an ether molecule.

Results (acrolein molecule)

a/ 2-state model

Using the simple model implying the forms |N> and |Z>:

$|N\rangle$ = D ━ A

$|Z\rangle$ = D^+ ━ A^-

the electronic ground state of the molecule can be expressed as:

$$|g\rangle = \sqrt{(1-\rho)}|N\rangle + \sqrt{\rho}|Z\rangle \quad (0 \leq \rho \leq 1)$$

with ρ the amount of charge transfer in the ground state (electron conjugation)

$$D^{+\rho} — A^{-\rho}$$

b/ Populations and charges π

	LCAO coeff pz	LCAO coeff pz	population pi	charge pi
(C1)	-0,1506	-0,6631	0,925	0,075
(O)	-0,769	0,3219	1,390	-0,390

The +M effect in the molecule in induced by the delocalisation of the π lone pair of the oxygen atom. Therefore, ρ can be evaluated as the π charge of the oxygen : ρ = –0.390. The ground state wavefunction is thus :

|g> = 0.7810|N> + 0,6245|Z>

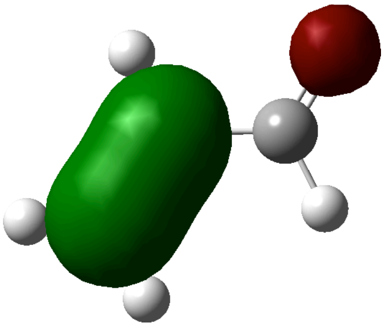
c/ π bond index between adjacent atoms

Atoms	Bond index
C1-C2	
C2-C3	0.234526
C3-C4	
C4-O	

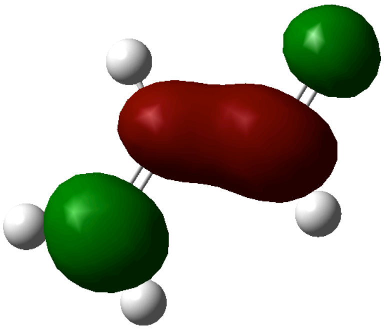
The non-zero values of the BI (2-3) and (4-O), and the values smaller than 1 for the BI (1-2) and (3-4), confirm the contribution of the zwitterionic form in the ground-state wavefunction.

d/ Frontier orbitals

HOMO-1



LUMO



F/ Photochromic systems

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

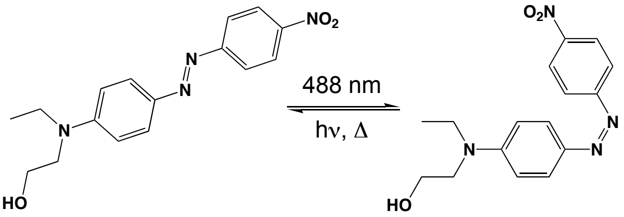


Figure 4: Cis-trans isomerization of DR1

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:

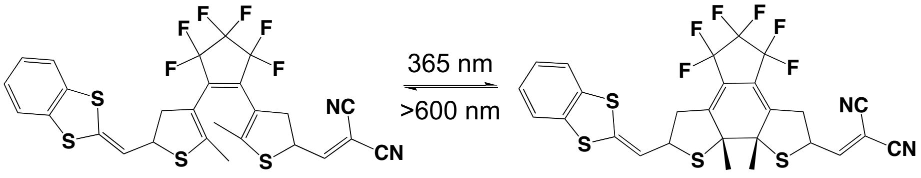


Figure 5: Photochromic equilibrium in a diarylethene derivative