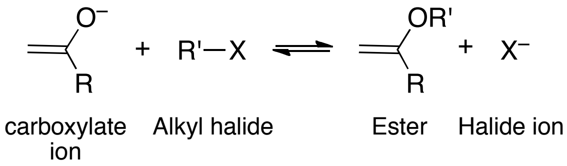
MMCO Projects

A list of computational projects is proposed below. The projects are labeled “PXi” with X the project number and i=a, b or c.

Projects PXa will be conducted at the AM1 level.
Projects PXb are the same as PXa but will be conducted at the PM3 level.
Projects PXc are the same as PXa but will be conducted at the PM6 level.

Project P1a: Relative Reactivity of Halide Leaving Groups in SN2 Reactions

We consider the SN$_2$ reaction implying a carboxylate ion and an alkyl halide.



Model this reaction at the AM1 level with R=R'=CH_3 and X = F, Cl, Br and I. Use the SM5.2 solvation model to account for solvent effects (acetone). Comment on the impact of X on the reactivity.

Project P2a: Solvent Effects in SN2 Reactions

We consider the SN$_2$ reaction implying an alkyl bromide and a lithium iodide.

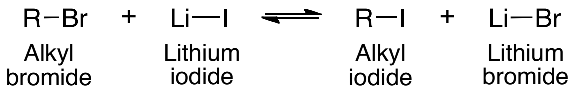
$$H_3CH_2C{-}I \quad + \quad CN^- \quad \rightleftharpoons \quad H_3CH_2C{-}CN \quad + \quad I^-$$

Model this reaction at the AM1 level by using the SM5.2 solvation model to account for solvent effects. Check the impact of varying the nature of the solvent on the chemical reactivity.

Project P3a: Steric Effects and SN2 Reaction Rates

Important note: ELEMENT Li IS NOT VALID IN A AM1 CALCULATION. The P3a project will be conducted at the MNDO level.

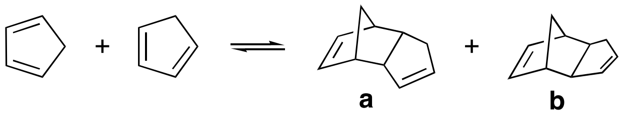
We consider the SN$_2$ reaction implying an alkyl bromide and a lithium iodide.



Model this reaction at the MNDO level by considering a methyl, ethyl, isopropyl, and tert-butyl bromide. Use the SM5.2 solvation model to account for solvent effects (acetone). Comment on the impact of the steric hindrance on the reactivity.

Project P4a: Diels-Alder [4+2] Cyclo-addition

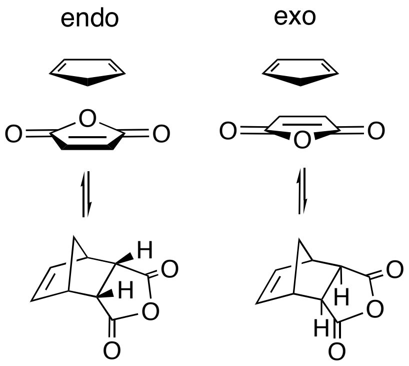
We consider the Diels Alder [4+2] addition below.



Model the Diels Alder additions leading to products **a** and **b** at the AM1 level, and check whether the computational results are consistent with the selectivity predicted by using the frontier orbital model.

Project P5a: Diels-Alder [4+2] Cyclo-addition

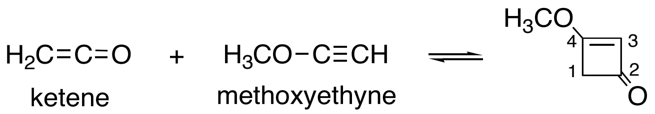
We consider the Diels Alder [4+2] addition between the maleic anhydride and the cyclopentadiene.



Model the Diels Alder additions leading to the endo- and exo-products at the AM1 and at the AM1-D3H4 levels. Check whether the computational results are consistent with the selectivity predicted by using the frontier orbital model and with the reported experimental data. *Note: Calculations might be further refined using DFT. Ask for help.*

Project P6a: Diels-Alder [2+2] Cyclo-addition

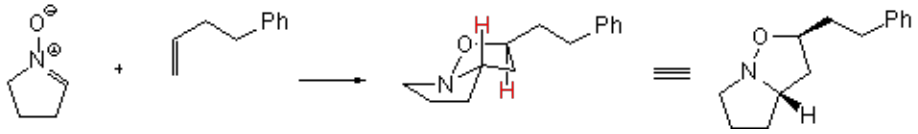
We consider the [2+2] addition of the ketene onto the methoxyethyne, in which the formation of the two C-C bonds is non-synchronous.



Model the reaction at the AM1 level by considering that i) the C1-C4 bond is formed first, and ii) the C2-C3 bond is formed first. Check which mechanism is the most favorable kinetically.

Project P7a: 1,3 dipolar Cyclo-addition

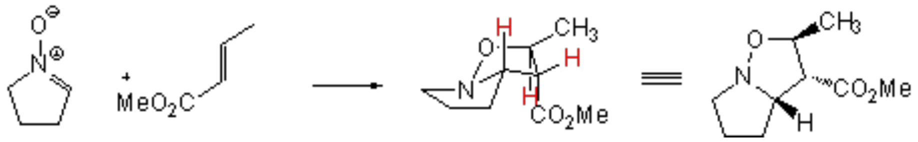
We consider the 1,3 dipolar cyclo-addition below.



Model the reactions leading to the endo- and exo-products at the AM1 level, and check whether the computational result are consistent with the selectivity predicted by using the frontier orbital model.

Project P8a: 1,3 dipolar Cyclo-addition

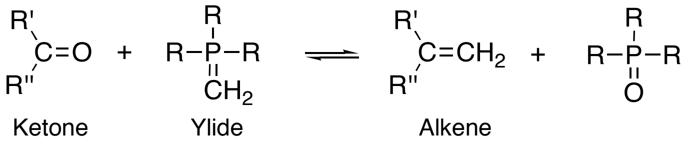
We consider the 1,3 dipolar cyclo-addition below.



Model the reactions leading to the endo- and exo-products at the AM1 level, and check whether the computational result are consistent with the selectivity predicted by using the frontier orbital model.

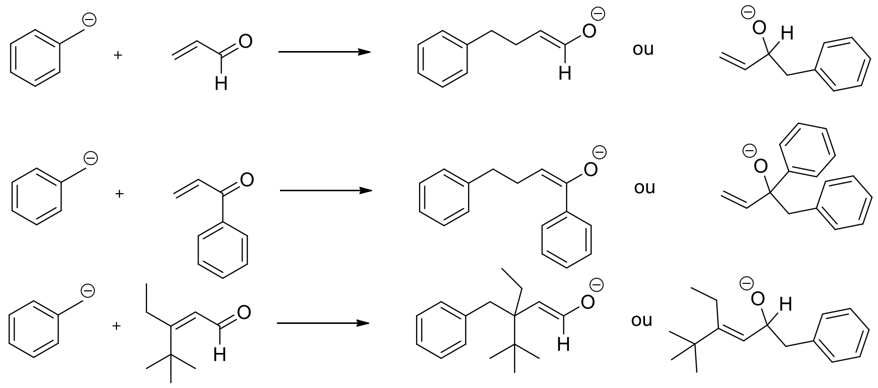
Project P9c: The Wittig Reaction

The Wittig Reaction allows the preparation of an alkene by the reaction of an aldehyde or ketone with the ylide generated from a phosphonium salt. Model the reaction below at the PM6 level with R’=R”=H and R = Me and Ph. Compare the chemical reactivity in the two cases. *The project will be conducted at the PM6 level only.*



Project P10a: The Michael addition reaction

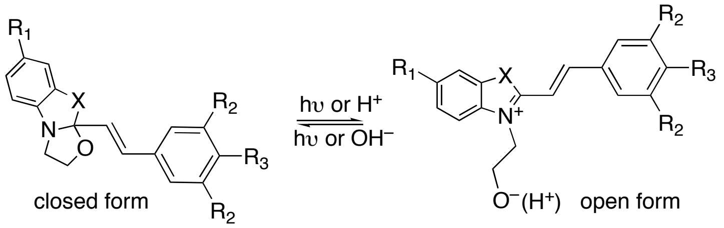
The Michael reaction or Michael addition is the nucleophilic addition of a carbanion or another nucleophile to an α,β-unsaturated carbonyl compound. Model the reactions below at the AM1 level and comment on the kinetics of the reaction mechanism in the three cases.



Project P11a: Absorption properties of photochromic molecules

Benzazolo-oxazolidine derivatives (Scheme below) are photochromic systems, which have the ability to commute indifferently upon light irradiation or pH variations. The photochromic process implies the breaking of a σ-bond on the oxazolidine moiety, leading to the formation of a colored zwitterionic form. The geometrical relaxation induced by the oxazolinic ring opening leads to an improved electron conjugation/delocalization along the molecule, responsible for the change in optical signatures. Upon acidic addition, a protonated open form (POF) is generated, whose absorption spectrum is identical to that of the zwitterionic form.

Total back photo-bleaching is achieved either by irradiation of the zwitterionic forms with an appropriate visible light, or by base addition on the POF.



a X=CMe$_2$ R$_1$=R$_2$=H R$_3$=OMe
b X=CMe$_2$ R$_1$=H R$_2$=R$_3$=OMe
c X=CMe$_2$ R$_1$=R$_2$=H R$_3$=NMe$_2$
d X=CMe$_2$ R$_1$=NO$_2$ R$_2$=H R$_3$=NMe$_2$

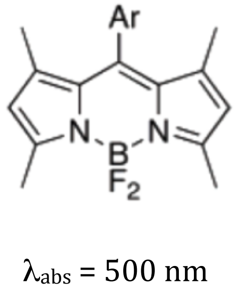
Model the absorption properties of compounds **a** and **b** in their closed and protonated open forms at the AM1 level, by using the Configuration Interaction method including only single electron excitations (SCI). Compare your results to experimental data (J. Phys. Chem. B, **2005**, *109*, 11139 ; Chem. Eur. J., **2009**, *15*, 2560).

Project P12a: Absorption properties of photochromic molecules

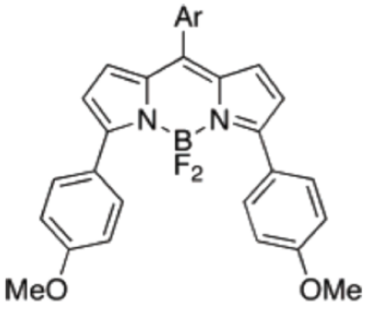
Same as project P11a, for compounds **c** and **d**.

Project P13a: Absorption and emission properties of BODIPY dyes

Calculate the absorption and emission wavelengths, as well as the associated Stocke shift (in cm^{-1}) for the two BODIPY derivatives schematized below at the AM1/CIS level with an active space of 20 molecular orbitals. Comment on the impact of the 3,5-substitution on the spectroscopic properties and compare to the experimental data [A. Loudet, K. Burgess, Chem. Rev. 107, 4891 (2007)].



λ_{abs} = 500 nm
λ_{em} = 510 nm
Φ = 0.64



λ_{abs} = 582 nm
λ_{em} = 626 nm
Φ = 0.42