Radiationless relaxation pathways in molecular dimers

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The role of the radiationless relaxation in photochemistry

Quantum Yield (Φ) measurements for dopamine:

pH	Solution	QY (%)
5.5	Concentrated Diluted	3.4 3.4
8.0	Concentrated Diluted	2.0 2.4

$$\Phi = \frac{Nr.\,Photons\ Emitted}{Nr.\,Photons\ Absorbed} = \frac{k_r}{k_r + k_{nr}}$$

For ex. for **Φ=2.0**, the non-radiation process is **50** times faster than the radiation one !!!

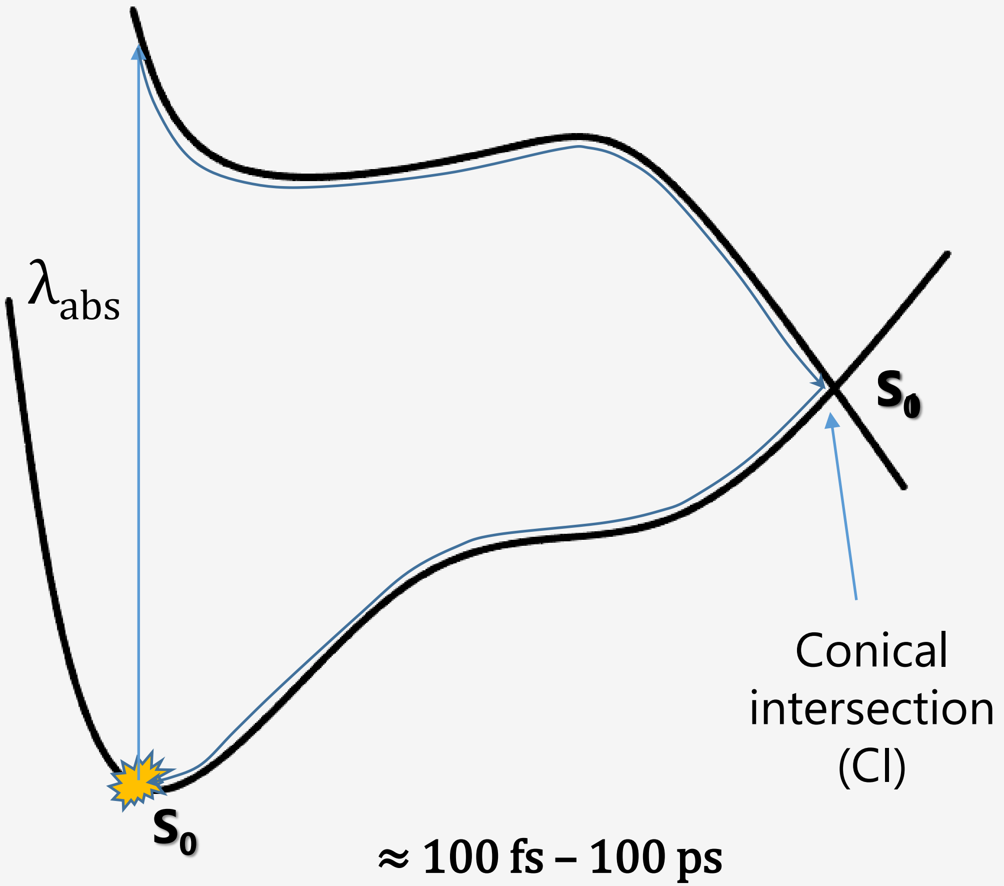
The role of the radiationless relaxation in photochemistry

	Name:	Time scale:
Non-radiative processes	Internal conversion (IC)	10^{-14} - 10^{-11} s
	Intersystem crossing (ISC)	10^{-8} - 10^{-3} s
	Excited state energy and charge transfer	10^{-14} - 10^{-13} s
Multi-step processes	Förster or fluorescence resonance energy transfer (FRET)	
	Triplet-triplet annihilation (TTA)	
	Singlet fission	

The most general radiationless relaxation of a molecule is an "*internal conversion*" transition through the so-called **conical intersection** geometries.

The role of the radiationless relaxation in photochemistry

Internal conversion: is a radiationless transition between energy states of the same spin state



The role of the radiationless relaxation in photochemistry

Theoretical methods: - Strong static electron correlation effects due to the degenerated electronic states.

➡ Needs for multiconfigurational (multi-determinant) electronic structure methods:
MCSCF, MRPT2, NEVPT2, etc.

TDDFT ??? - In principle, is an one-determinant theory (like Hartree-Fock), but in the exchange-correlation functionals could be include also some terms to cover these effects.

In TDDFT the $\chi(\mathbf{r}, \mathbf{r}', \omega)$ response function contains the Ω_n excitation energies as poles of a complex function:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) \approx \sum_{n=1}^{\infty} \left\{ \frac{(\cdots)}{\omega - \Omega_n + i\eta} - \frac{(\cdots)}{\omega + \Omega_n + i\eta} \right\}$$

If S_1 crosses S_0, one of the poles $\approx \frac{1}{0} \rightarrow \infty$

➡ Wrong dimensionality of the potential energy surface around the CI geometries !!!

The role of the radiationless relaxation in photochemistry

Solution: ⇨ Spin-flipped time-dependent density functional theory (SF-TDDFT).

The reference (ground state) calculation is the ground triplet state.

```
(SPIN-FLIP GROUND STATE)
STATE  1:  E=   0.033860 au      0.921 eV     7431.4 cm**-1 <S**2> =   1.968551
    19a ->  21b  :     0.027181 (c= -0.16486660)
    20a ->  20b  :     0.311919 (c= -0.55849705)
    21a ->  21b  :     0.604300 (c= -0.77736722)
    21a ->  22b  :     0.020863 (c=  0.14443910)

STATE  2:  E=   0.035624 au      0.969 eV     7818.6 cm**-1 <S**2> =   0.258584
    21a ->  20b  :     0.974742 (c=  0.98729028)

STATE  3:  E=   0.035645 au      0.970 eV     7823.2 cm**-1 <S**2> =   0.138335
    20a ->  20b  :     0.662083 (c=  0.81368483)
    21a ->  21b  :     0.288447 (c= -0.53707289)
```

STATE 1 ⇨ T_0

STATE 2 ⇨ S_0

STATE 3 ⇨ S_1

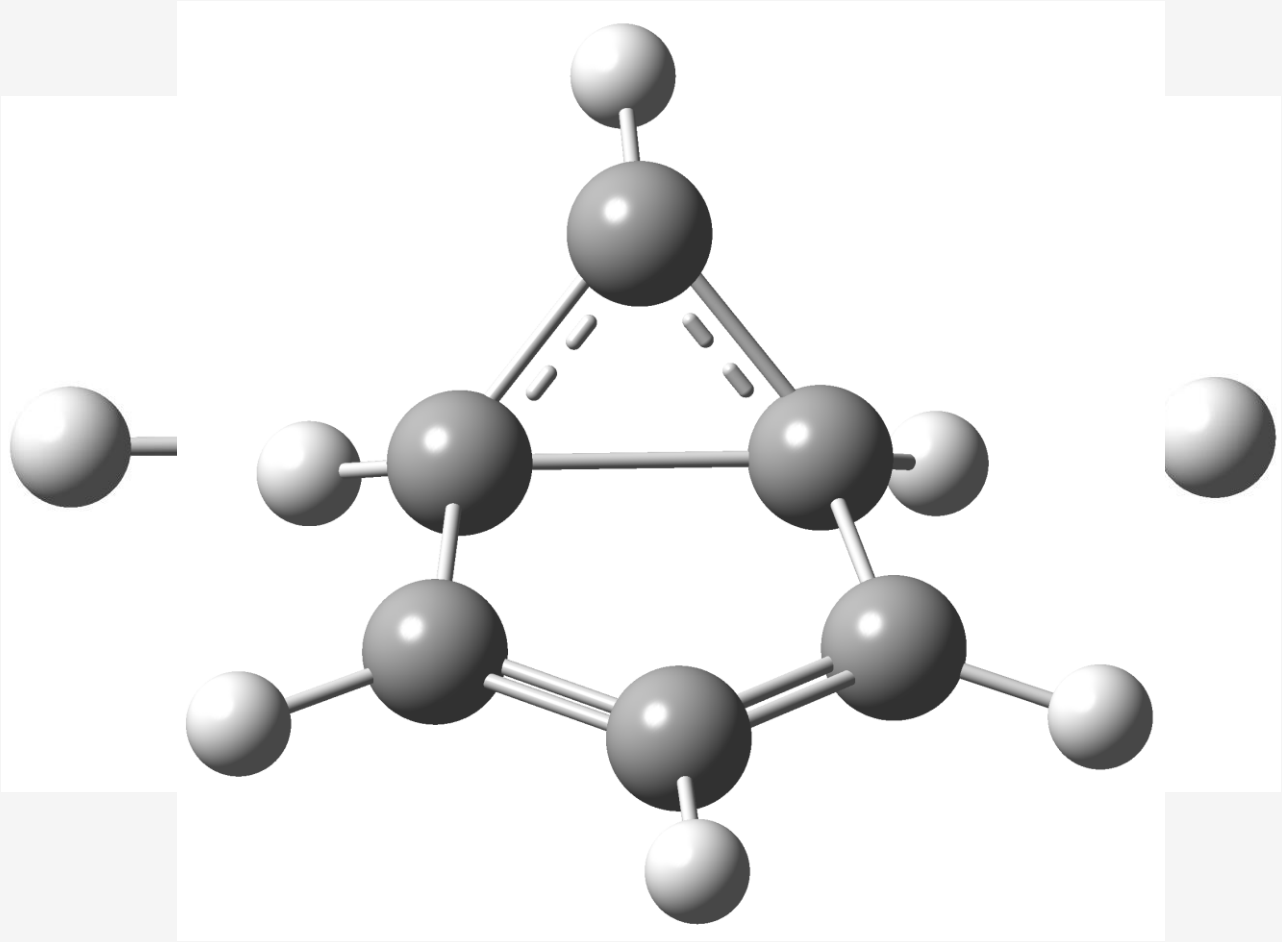
The case of benzene monomer and dimer

Benzene monomer: - The typical case study of aromatic molecules for conical intersection

Benzene ground state geometry

$S_0 \otimes S_1$ conical intersection geometry

Half-boat conformation



Conformational energy difference:

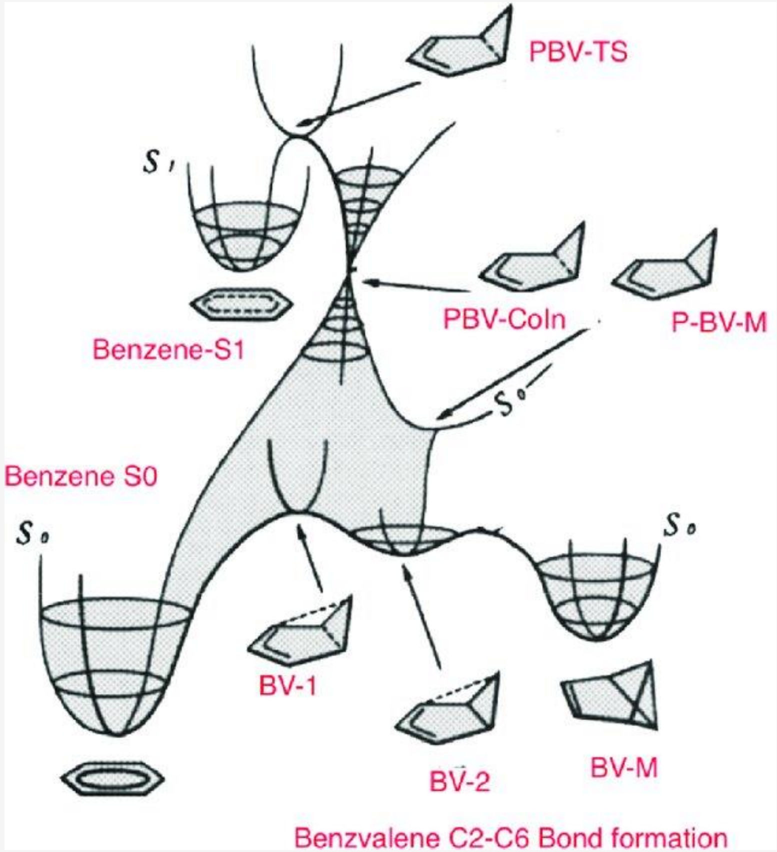
$\Delta(E^{CI} - E^{S0}) =$

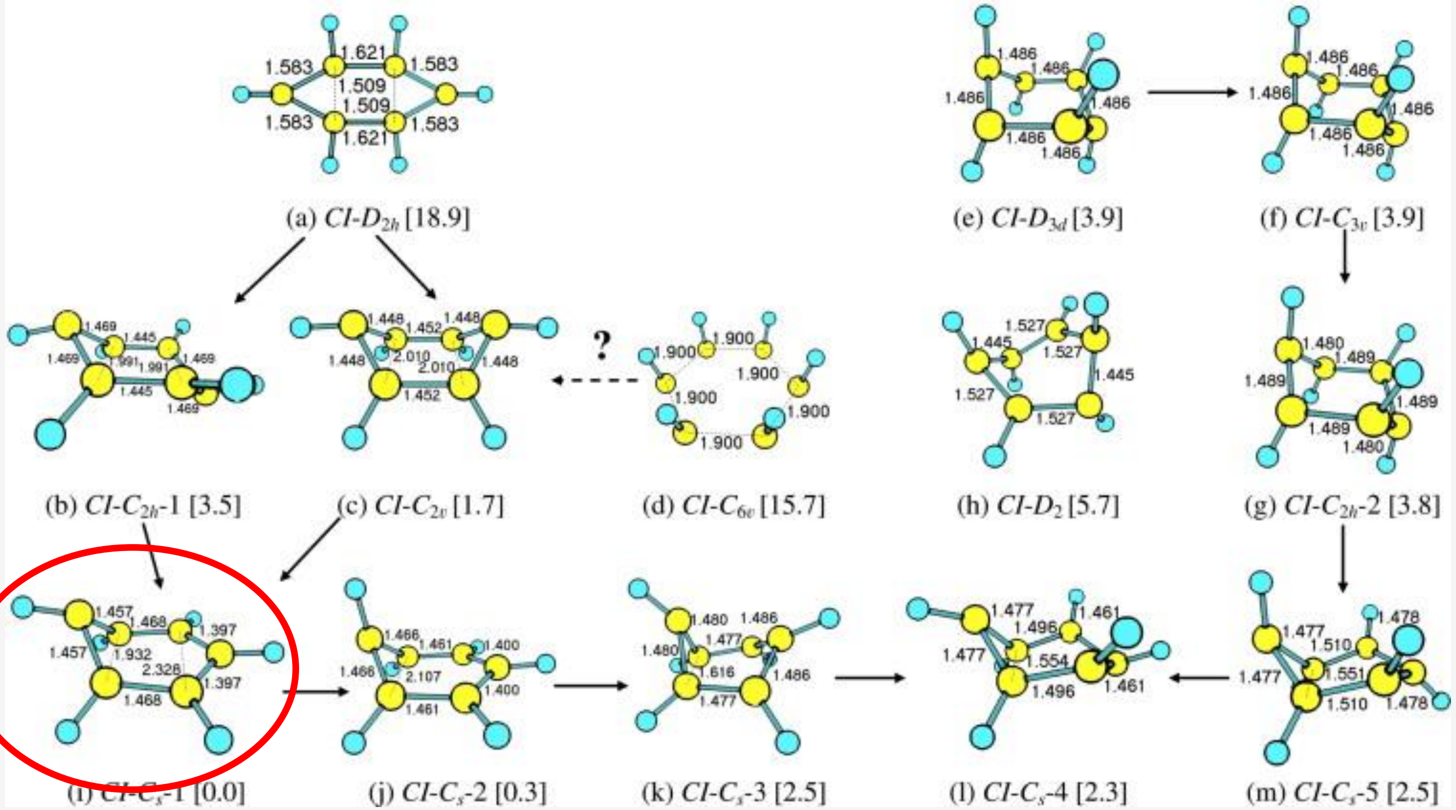
8.30 kcal/mol

ωB97X-D3/ma-def2-TZVPP

The case of benzene monomer and dimer

Benzene monomer:





Q. Li, D. Mendive-Tapia, M. J. Paterson, A. Migani, M. J. Bearpark, M. A. Robb, L. Blancafort, *Chem. Phys.* **377**(1–3), 60-65 (**2010**).

A. J. Jenkins, M. A. Robb, *Comput. Theor. Chem.*,**1152**, 53 (**2019**).

The case of benzene monomer and dimer

Benzene dimer: Method: spin-flipped TDDFT

Why? It also contains a significant amount of electron correlation effects

Through the D3 scheme it can be included dispersion effects

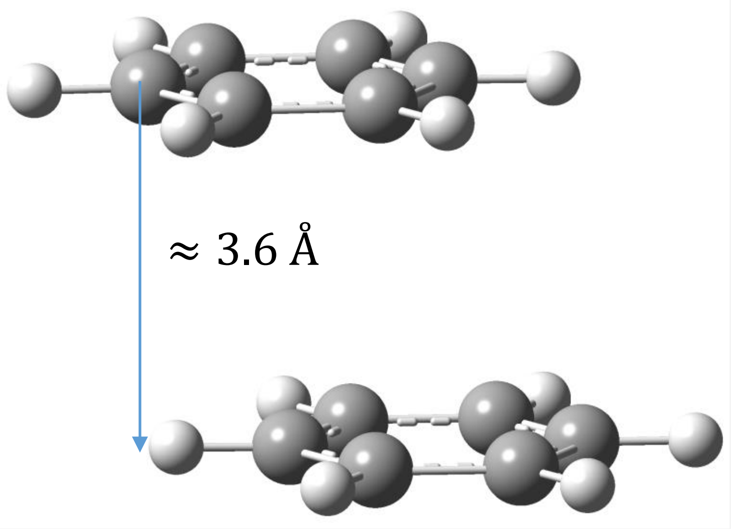
Multi-reference SCF does not contain dynamic electron correlation effects

Less computationally expensive

SF-TDDF/ωB97X-D3/ma-def2-TZVPP

The case of benzene monomer and dimer

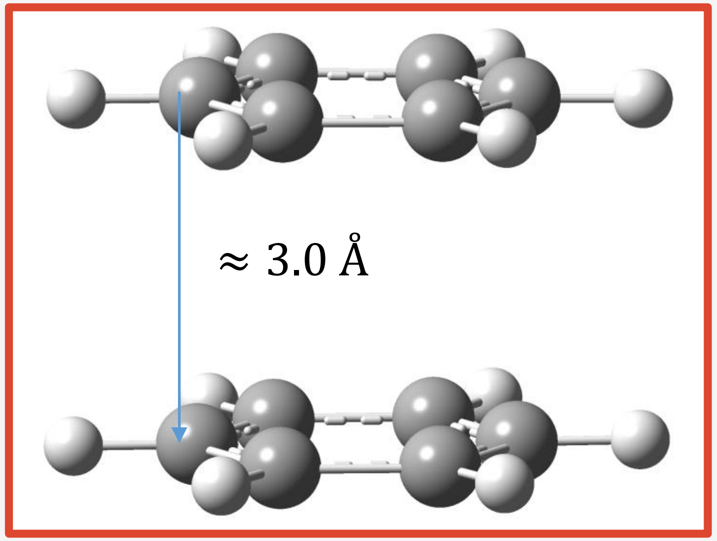
Benzene dimer:



Ground state

ΔE_{Int} = -3.14 kcal/mol

REF.



S_1 equilibrium geometry
(excimer)

ΔE_{Int} = -14.00 kcal/mol ➡ Strong hole – electron interaction

S_1 (monomer): 3.95 eV

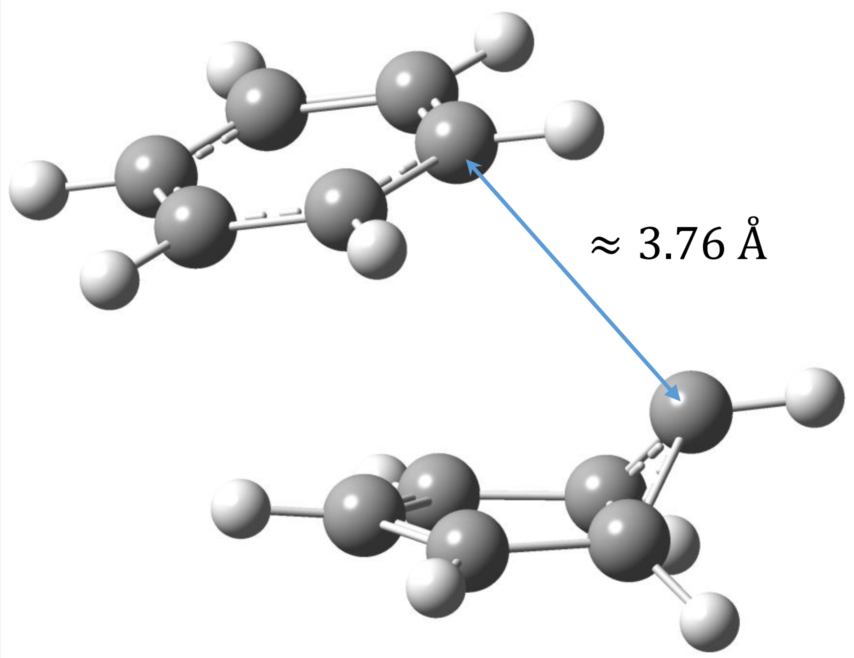
S_1 (dimer): 3.04 eV - excimer

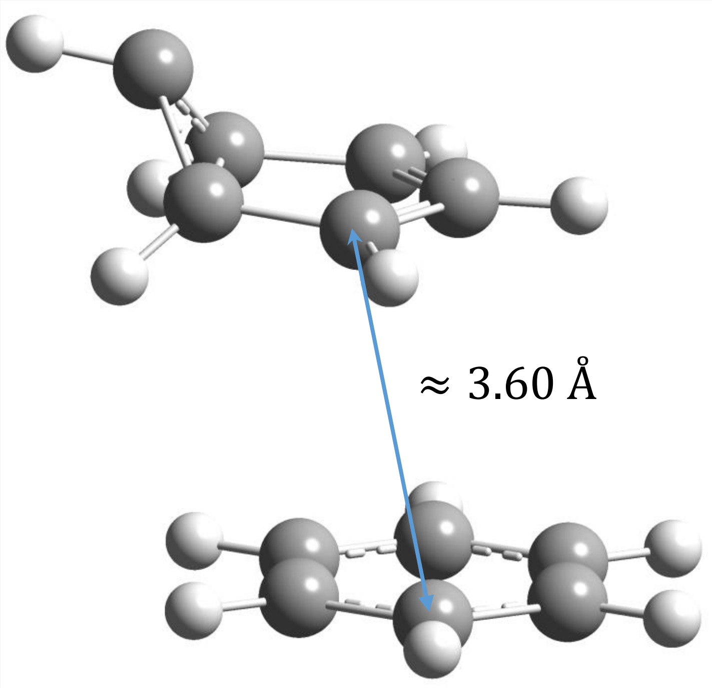
$\Delta E_{Int} = E_X - E_{REF}$

The case of benzene monomer and dimer

Conical intersection in benzene dimer:

A. Monomer deformation





ΔE_{Conf} = +17.60 kcal/mol

ΔE_{Conf} = +17.46 kcal/mol

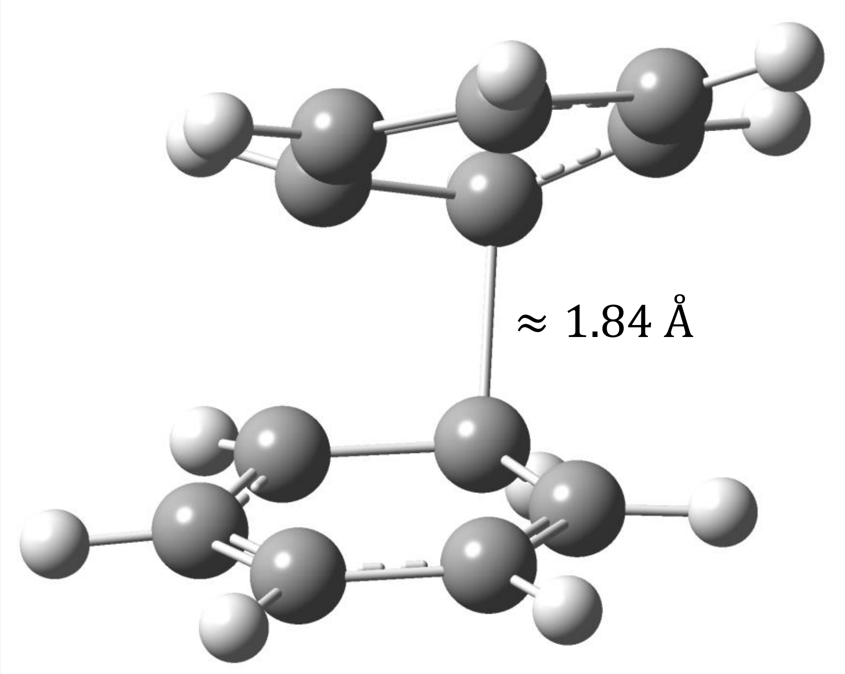
The case of benzene monomer and dimer

Conical intersection in benzene dimer:

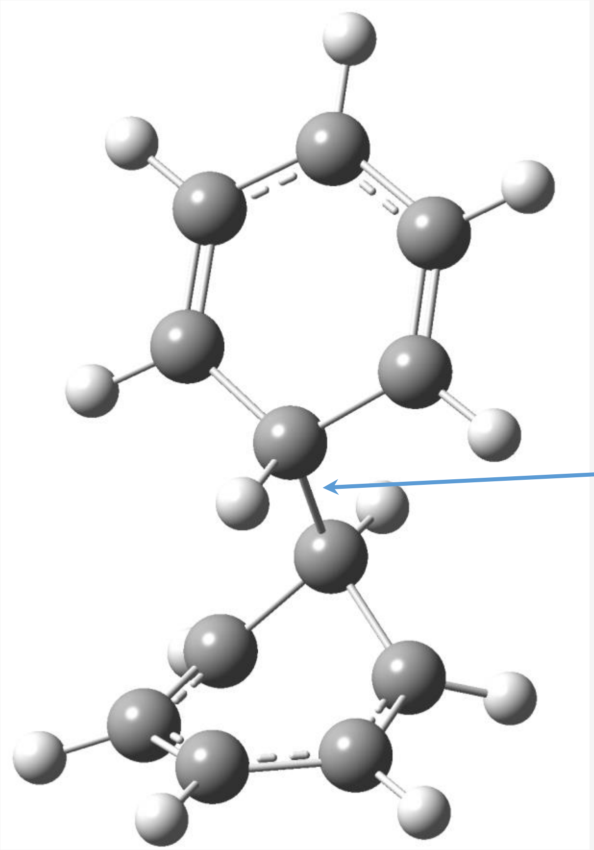
Method: SF-TDDF/ωB97X-D3/ma-def2-TZVPP

Results published in: A. Bende, A.-A.Farcaș, *Int. J. Mol. Sci.* **2023**, *24*, 2906.

B. Dimer deformation



ΔE_{Conf} = +1.00 kcal/mol



CI can be reached with much lower deformation energy over the monomers !!!

≈ 1.59 Å

ΔE_{Conf} = +1.18 kcal/mol

The case of benzene monomer and dimer

Conical intersection in benzene dimer:

Method: SF-TDDF/ωB97X-D3/ma-def2-TZVPP

B. Dimer deformation

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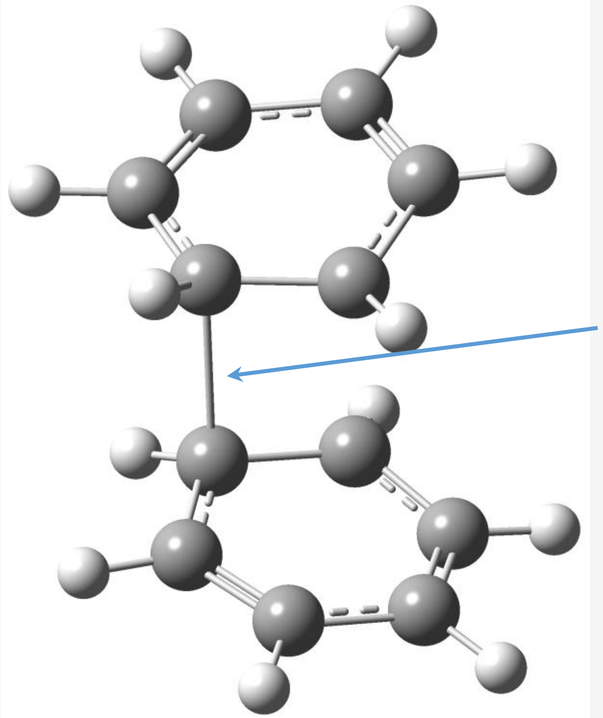
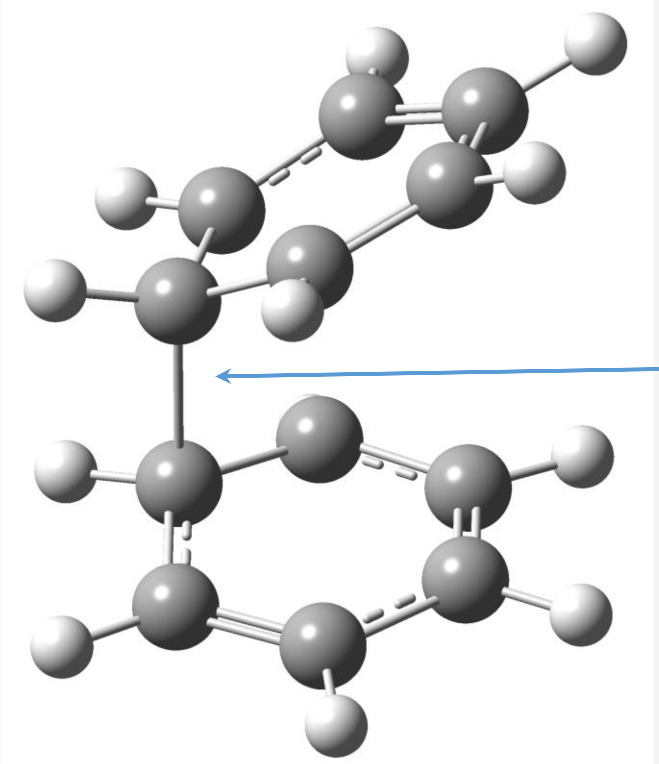


ΔE_{Conf} = +6.98 kcal/mol



ΔE_{Conf} = +7.54 kcal/mol

The case of benzene monomer and dimer

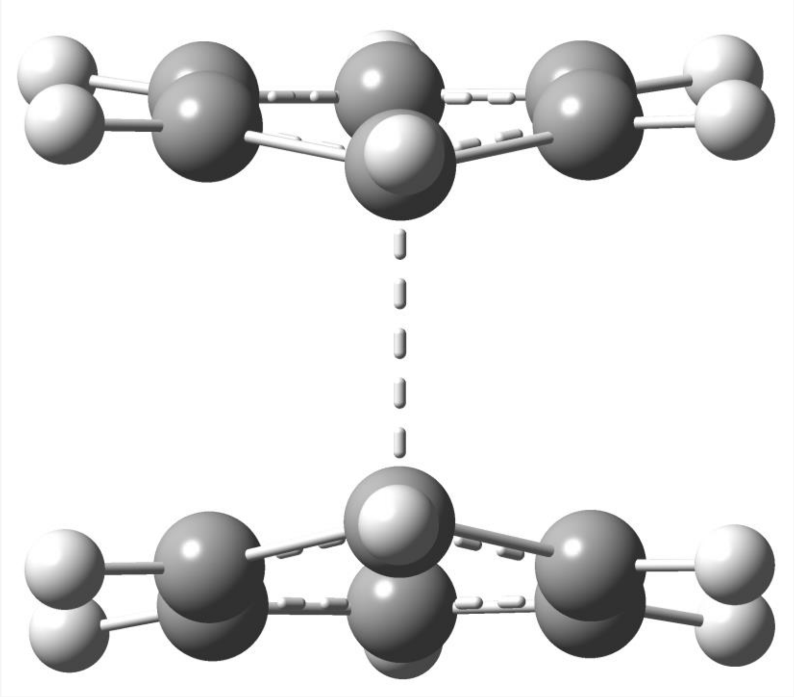
Conical intersection in benzene dimer:

Method: SF-TDDF/ωB97X-D3/ma-def2-TZVPP

C. Transition state: between R_e^{S1} and R_D^{CI}

Results published in: A. Bende, A.-A.Farcaș, *Int. J. Mol. Sci.* **2023**, *24*, 2906.

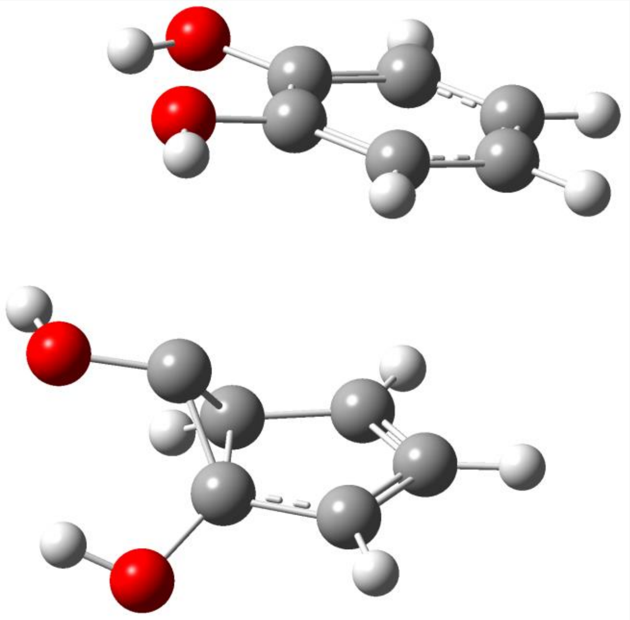
ΔE_{TS} = +7.54 kcal/mol

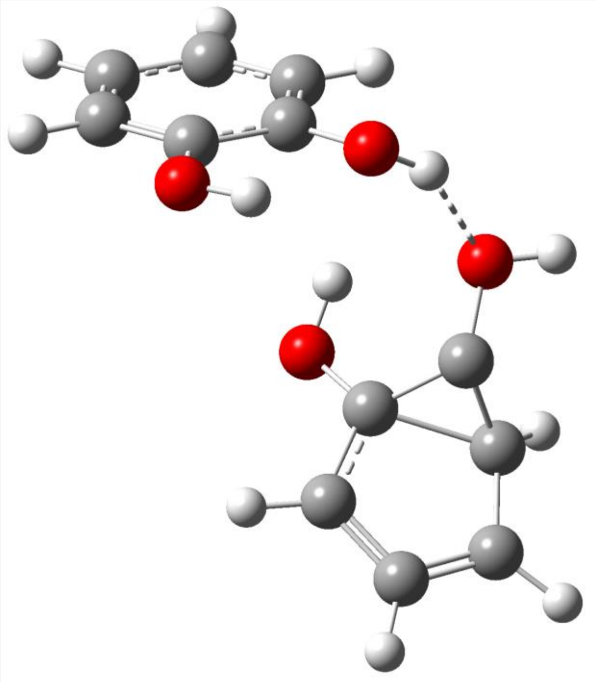


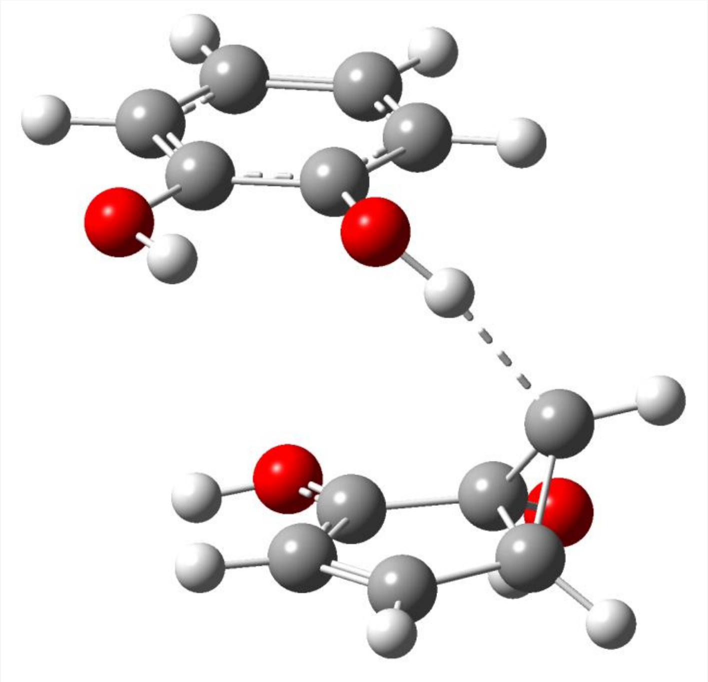
The case of catechol dimer

Conical intersection in catechol dimer:

Method: SF-TDDF/ωB97X-D3/ma-def2-TZVPP







ΔE_{Conf} = +25.23 kcal/mol

ΔE_{Conf} = +24.66 kcal/mol

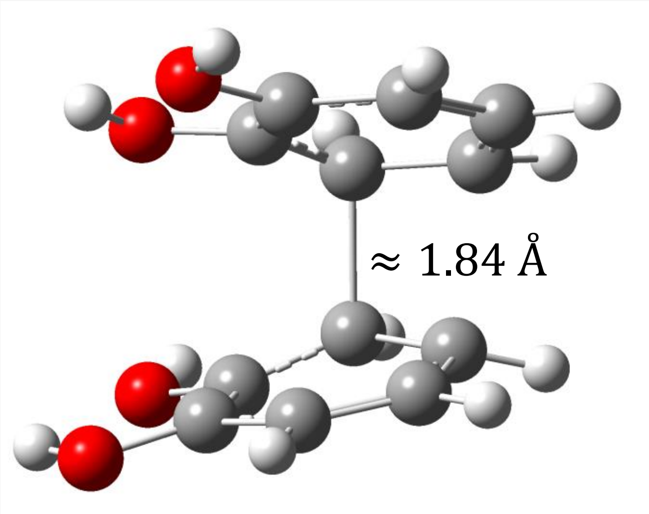
ΔE_{Conf} = +21.14 kcal/mol

Results published in: A. Bende, A.A. Farcaș, A. Falamaș, A. Petran, Phys. Chem. Chem. Phys., 2022, 24, 29165.

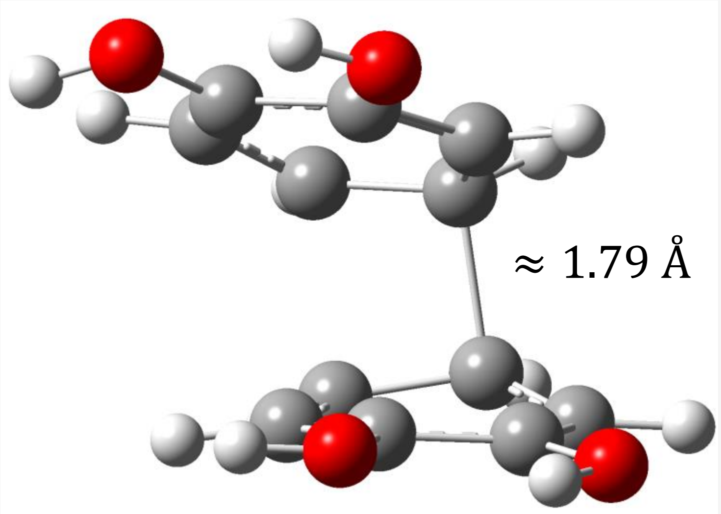
The case of catechol dimer

Conical intersection in catechol dimer:

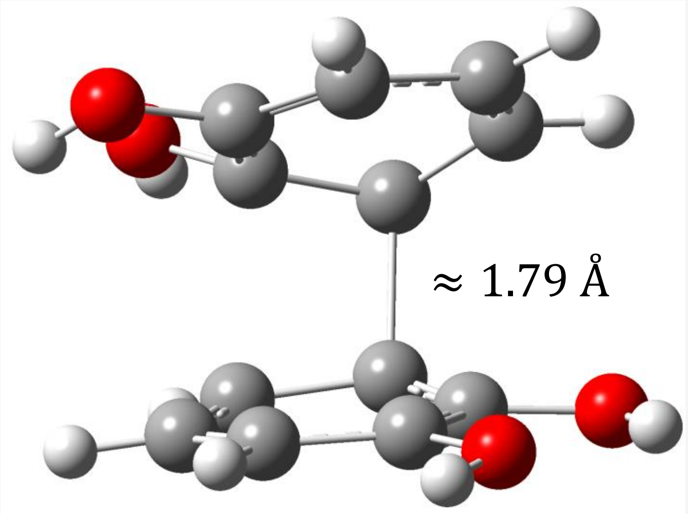
Method: SF-TDDF/ωB97X-D3/ma-def2-TZVPP



ΔE_{Conf} = +10.66 kcal/mol



ΔE_{Conf} = +11.20 kcal/mol

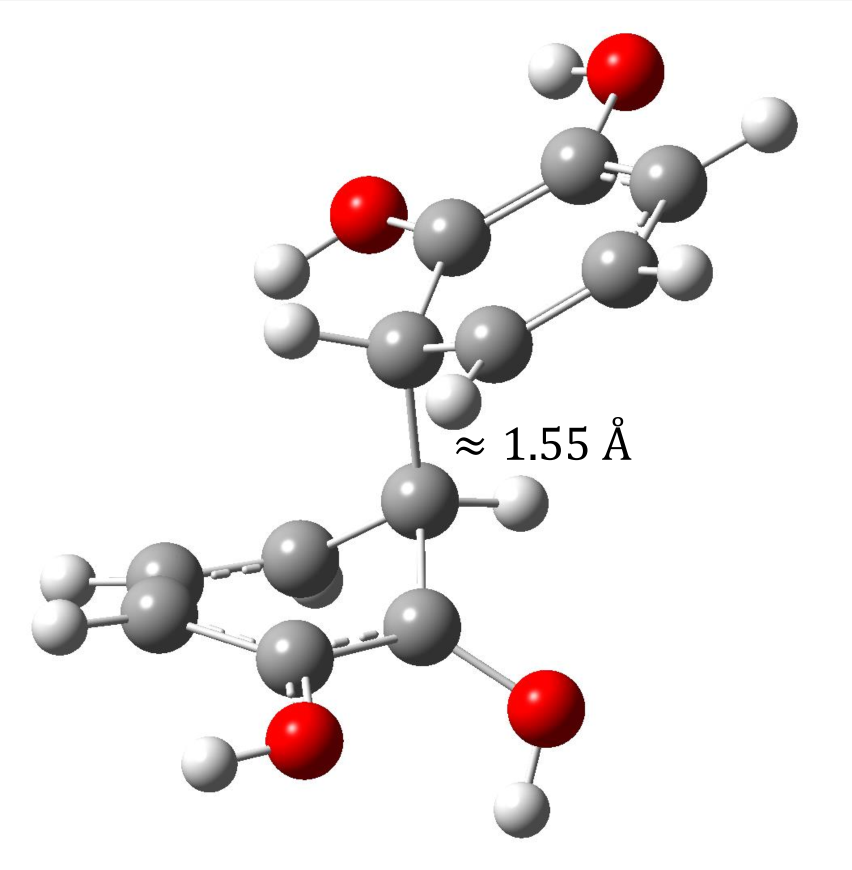


ΔE_{Conf} = +7.39 kcal/mol

Results published in: A. Bende, A.A. Farcaș, A. Falamaș, A. Petran, Phys. Chem. Chem. Phys., 2022, 24, 29165.

The case of catechol dimer

Conical intersection in catechol dimer:



Method: SF-TDDF/ωB97X-D3/ma-def2-TZVPP

ΔE_{Conf} = +13.08 kcal/mol

Results published in: A. Bende, A.A. Farcaș, A. Falamaș, A. Petran, Phys. Chem. Chem. Phys., 2022, 24, 29165.

Conclusions:

- Stronger intermolecular interaction energies between the monomers were found for the S_1 state than for the S_0 state;
- Dimer configurations in the S_1 electronic state prefer the perfect stacking geometry configuration instead of shifted-stacking or H-bonded forms;
- The dimer-type conical intersection geometries are energetically more favorable than the monomer-type CI configurations;
- The side fragments (OH groups) of the catechol can influence the conical intersection geometries and their energetics;

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Thank You for Your Attention