

# Molecular Modelling of Photochemical Properties in Molecules and Supramolecular Assemblies

Attila BENDE and Alex-Adrian FARCAȘ

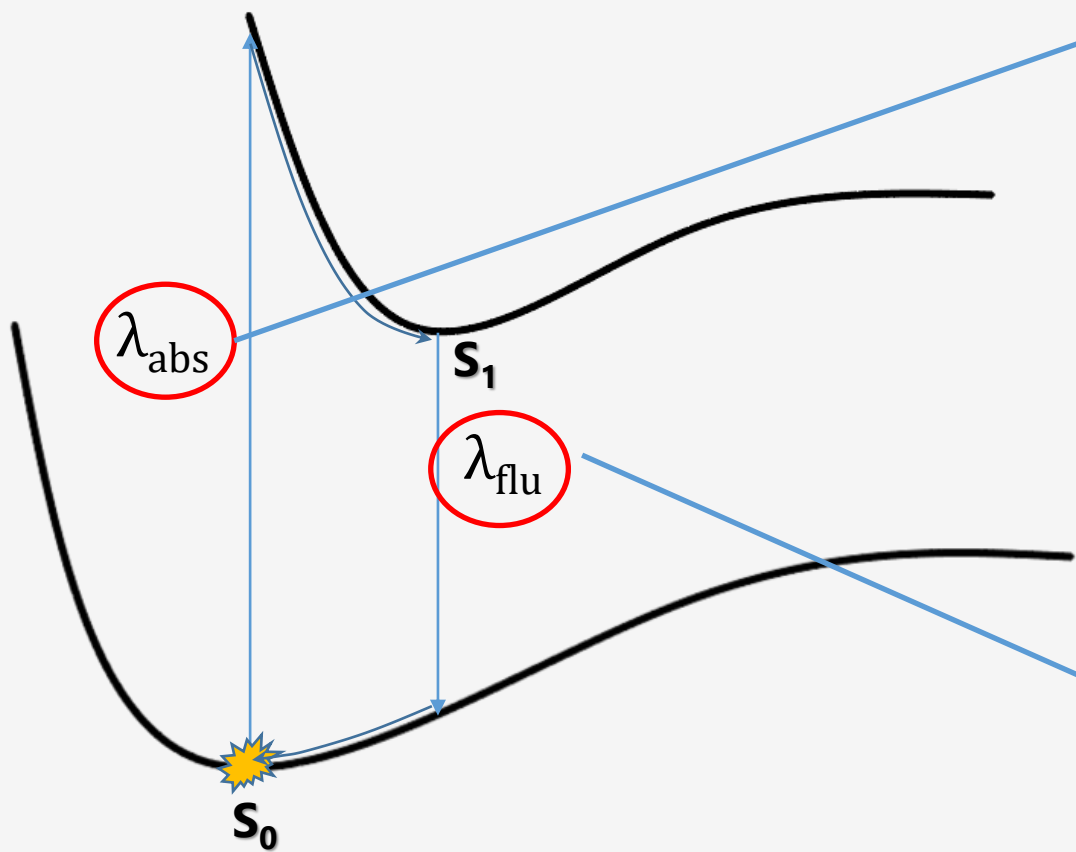
Molecular and Biomolecular Physics Department, National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

# Content

---

- 1 Principles of molecular photochemistry
- 2 The role of the radiationless relaxation in photochemistry
- 3 The case of benzene monomer and dimer
- 4 The case of catechol dimer
- 5 Conclusions

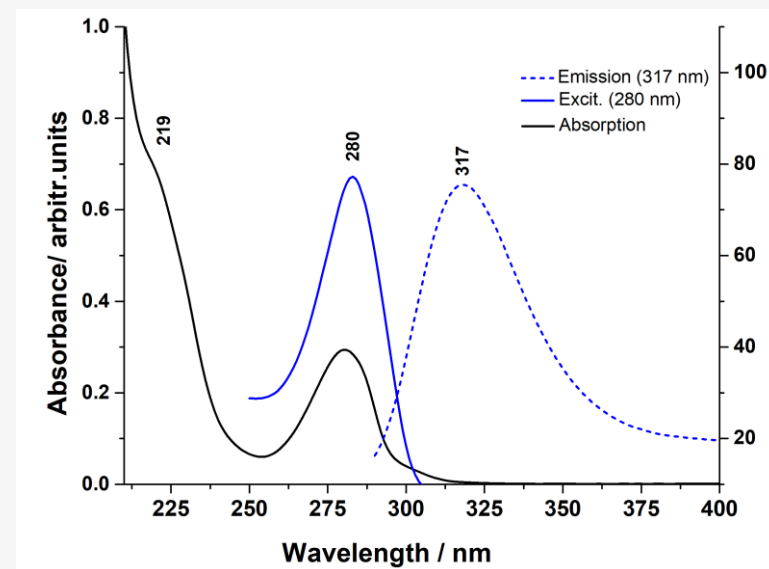
# Principles of molecular photochemistry



Time scale:  $\approx 100 \text{ ps} - 100 \text{ ns}$

UV-Vis absorption spectra

— Excit. — Absorption



Fluorescence spectra

- - - Flu. Emission

# The role of the radiationless relaxation in photochemistry

---

**Quantum Yield ( $\Phi$ )**  
measurements for  
dopamine:

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

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

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

# The role of the radiationless relaxation in photochemistry

---

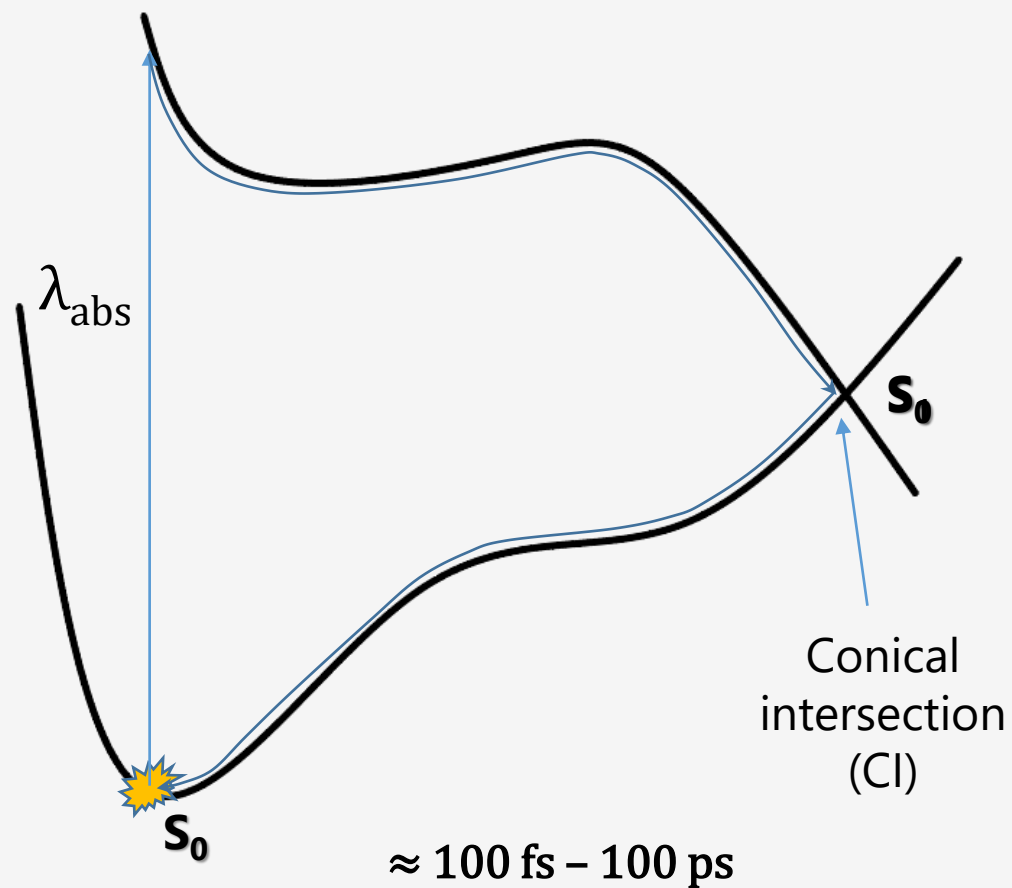
	<u>Name:</u>	<u>Time scale:</u>
Non-radiative processes	Internal conversion (IC)	$10^{-14} - 10^{-11} \text{ s}$
	Intersystem crossing (ISC)	$10^{-8} - 10^{-3} \text{ s}$
	Excited state energy and charge transfer	$10^{-14} - 10^{-13} \text{ s}$
Multi-step processes	Förster or fluorescence resonance energy 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  $\Omega_n$  excitation energies as poles of a complex function:

$$\chi(\mathbf{r}, \mathbf{r}', \omega) \approx \sum_{n=1}^{\infty} \left\{ \frac{(\dots)}{\omega - \Omega_n + i\eta} - \frac{(\dots)}{\omega + \Omega_n + i\eta} \right\} \quad \text{If } S_1 \text{ crosses } S_0, \text{ one of the poles } \approx \frac{1}{0} \rightarrow \infty$$

➔ 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 <sup>-1</sup>	<S <sup>2</sup> > =	1.968551		<b>T<sub>0</sub></b>
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 <sup>-1</sup>	<S <sup>2</sup> > =	0.258584		<b>S<sub>0</sub></b>
21a ->	20b	:	0.974742	(c= 0.98729028)				
STATE 3:	E=	0.035645 au	0.970 eV	7823.2 cm <sup>-1</sup>	<S <sup>2</sup> > =	0.138335		<b>S<sub>1</sub></b>
20a ->	20b	:	0.662083	(c= 0.81368483)				
21a ->	21b	:	0.288447	(c= -0.53707289)				

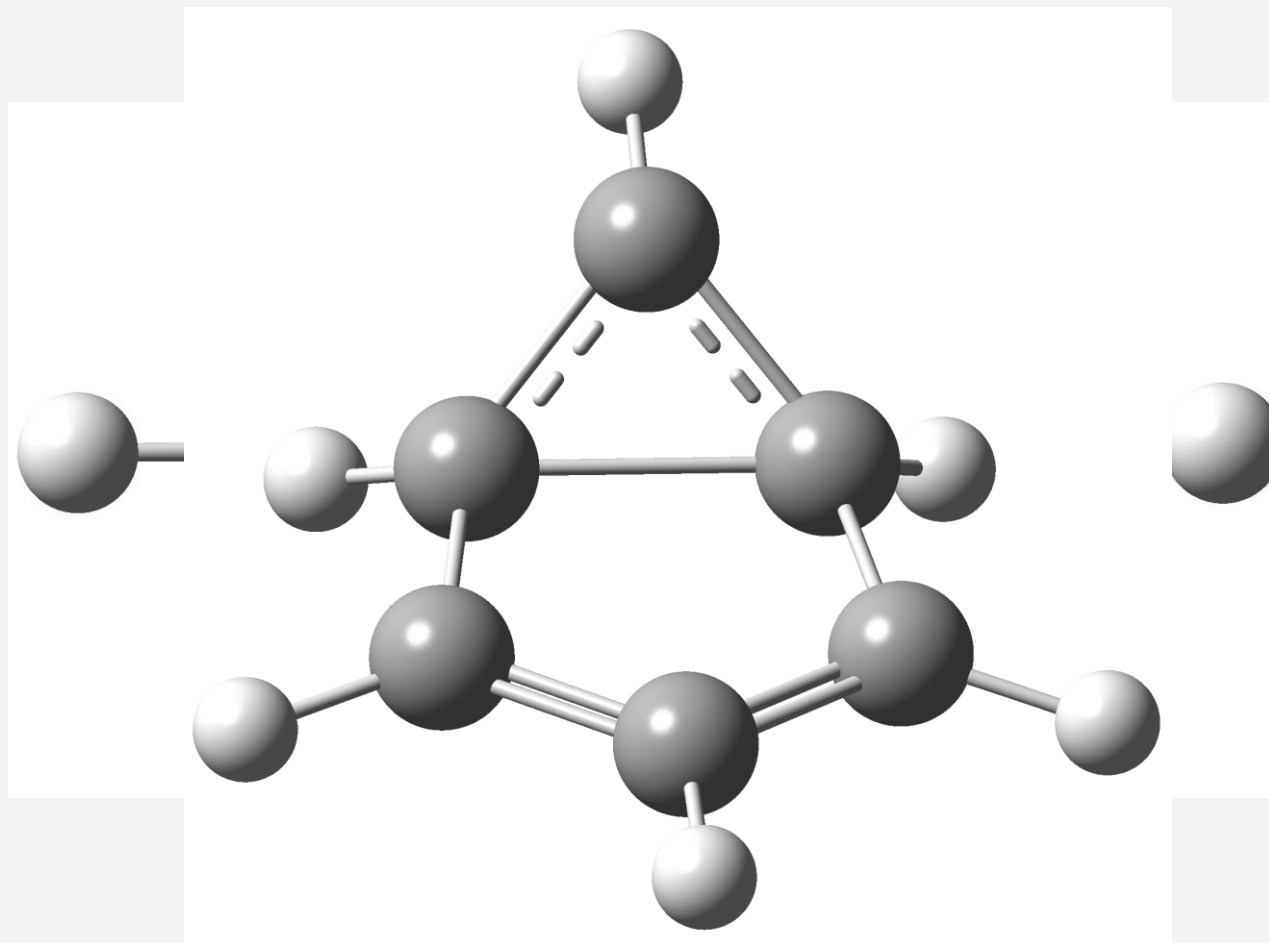


# The case of benzene monomer and dimer

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

Benzene  $S_0$  and  $S_1$  static intersection geometry

Half-boat conformation



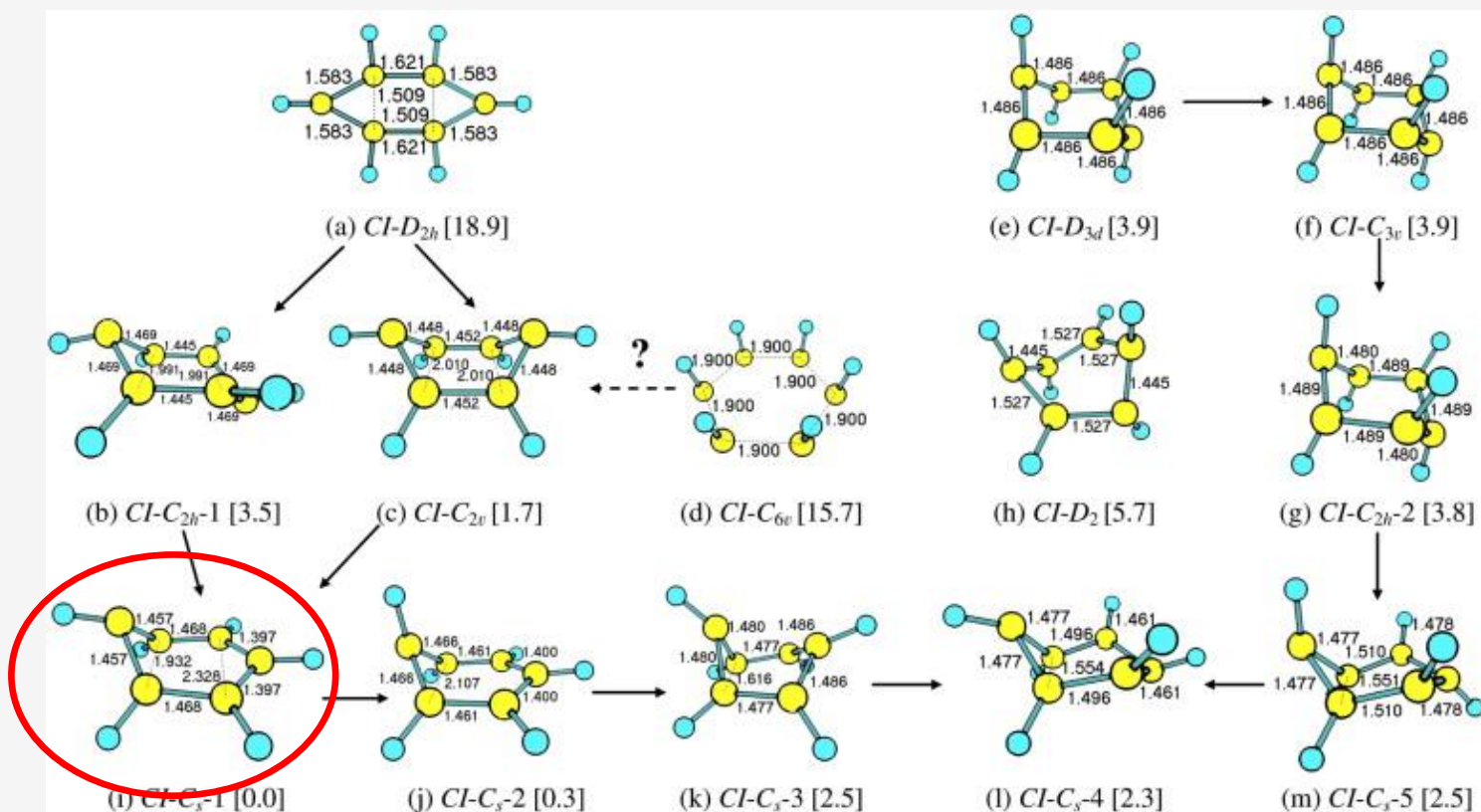
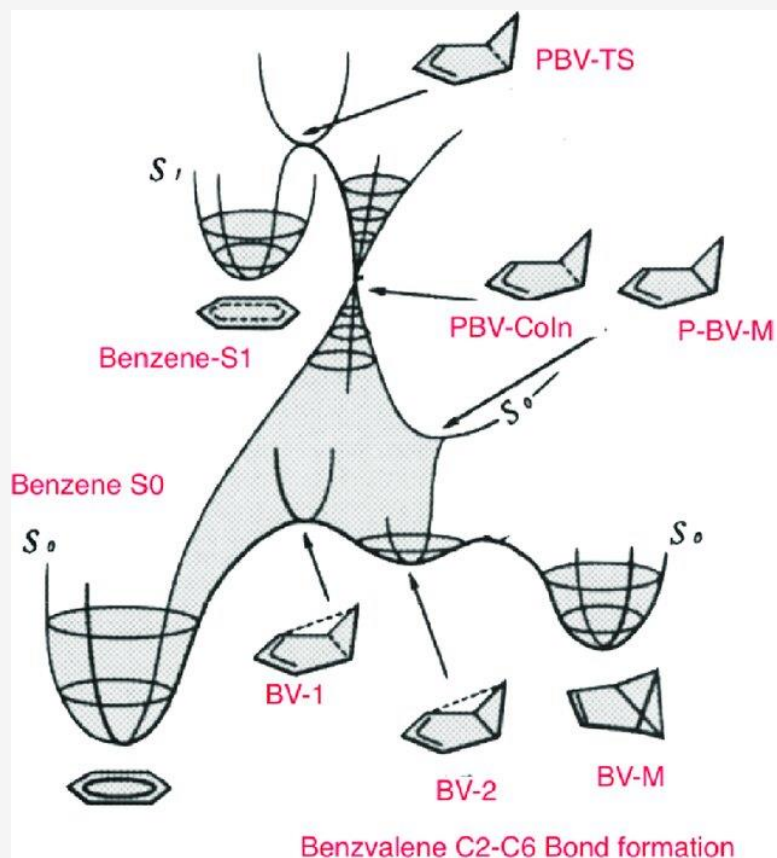
Conformational energy difference:

$$\Delta(E^{\text{CI}} - E^{S_0}) = 8.30 \text{ kcal/mol}$$

$\omega$ B97X-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

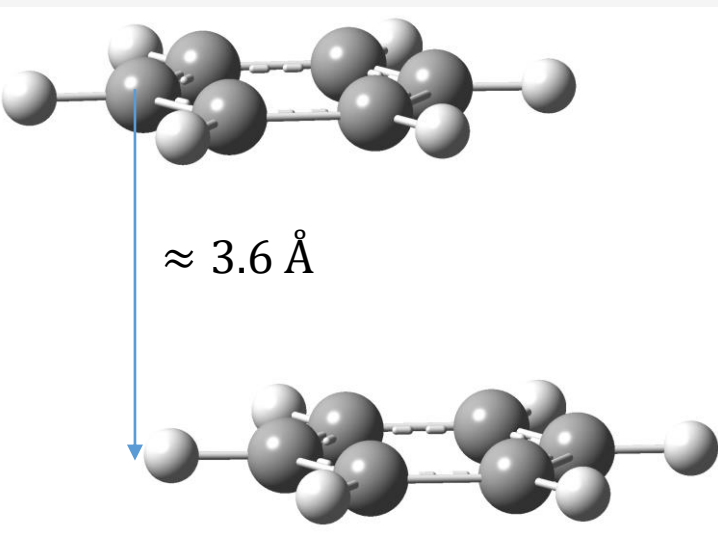
Multi-reference SCF does not contain dynamic electron correlation effects

Less computationally expensive

SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP

# The case of benzene monomer and dimer

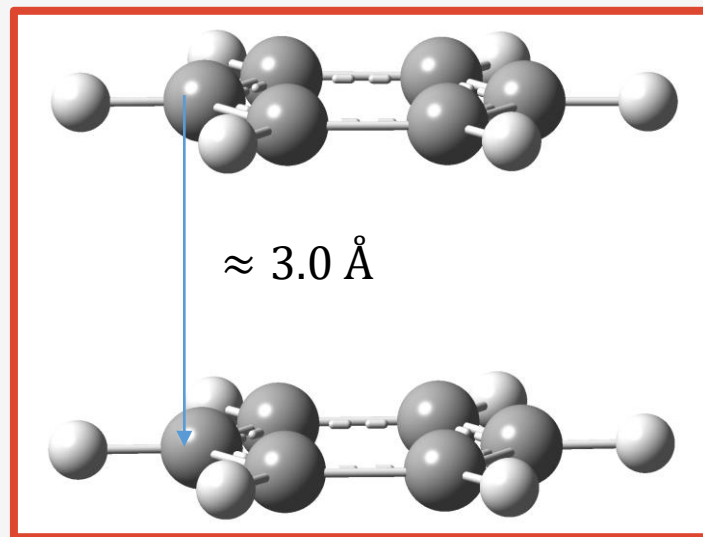
## Benzene dimer:



Ground state

$$\Delta E_{\text{Int}} = -3.14 \text{ kcal/mol}$$

## REF.



$S_1$  equilibrium geometry  
(excimer)

$$\Delta E_{\text{Int}} = -14.00 \text{ kcal/mol} \rightarrow \text{Strong hole - electron interaction}$$

$S_1$  (monomer): 3.95 eV

$S_1$  (dimer): 3.04 eV - excimer

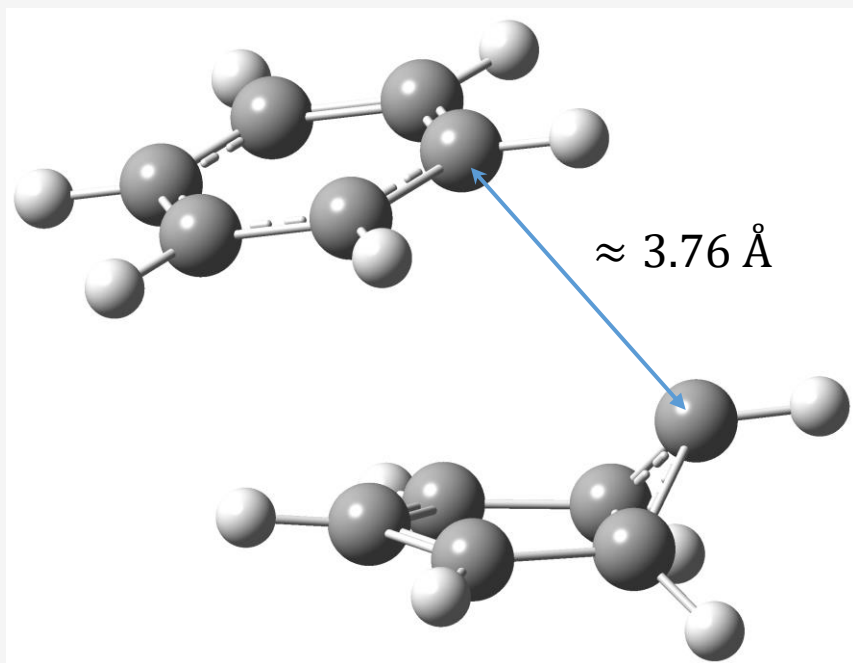
$$\Delta E_{\text{Int}} = E_X - E_{\text{REF}}$$

# The case of benzene monomer and dimer

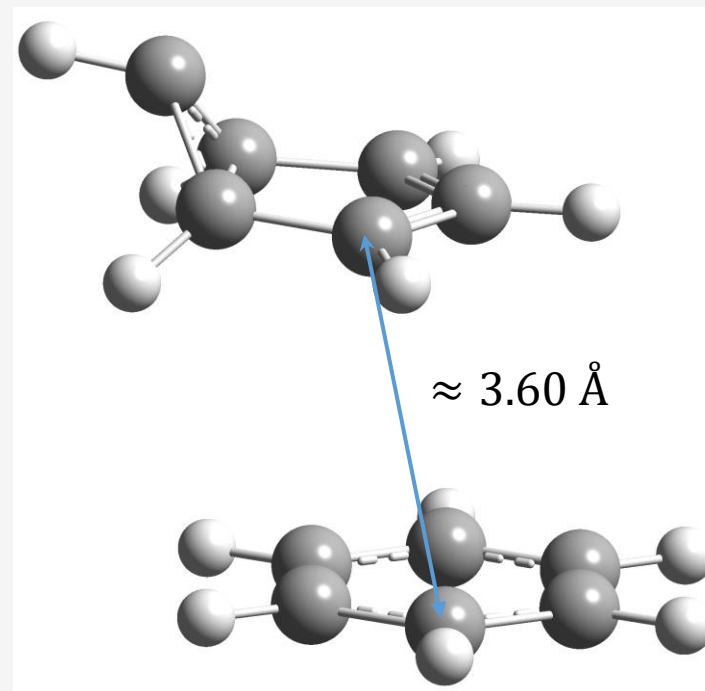
---

## Conical intersection in benzene dimer:

### A. Monomer deformation



$$\Delta E_{\text{Conf}} = +17.60 \text{ kcal/mol}$$



$$\Delta E_{\text{Conf}} = +17.46 \text{ kcal/mol}$$

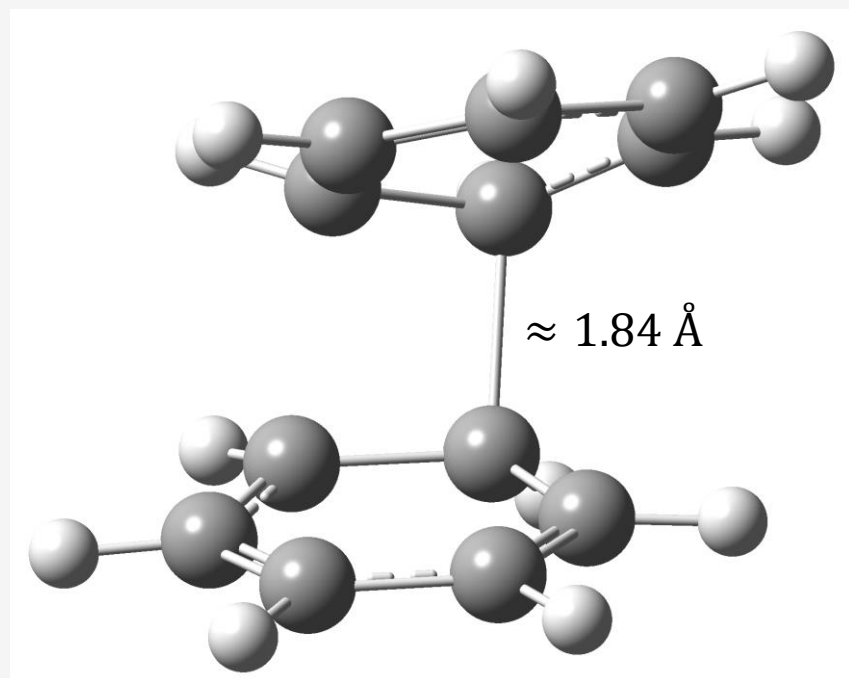
# The case of benzene monomer and dimer

## Conical intersection in benzene dimer:

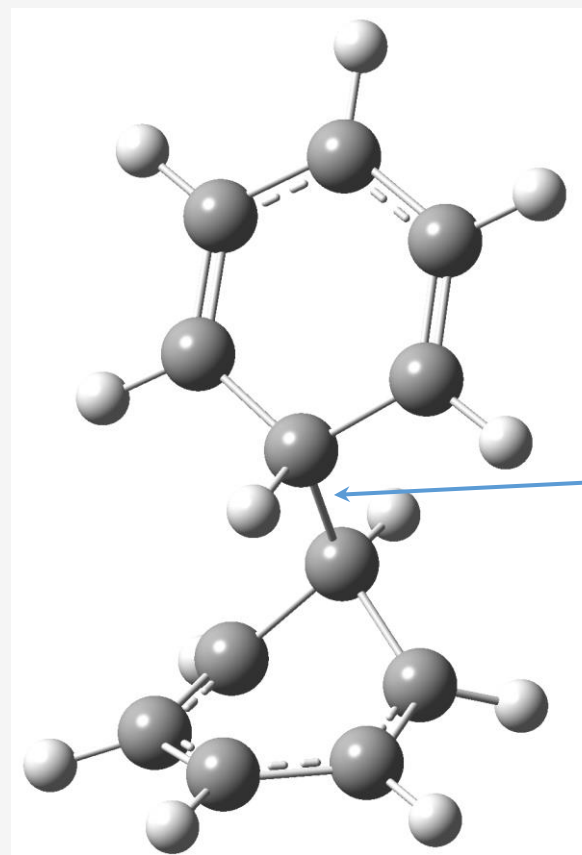
Method: SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP

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

### B. Dimer deformation



$$\Delta E_{\text{Conf}} = +1.00 \text{ kcal/mol}$$



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

$$\Delta E_{\text{Conf}} = +1.18 \text{ kcal/mol}$$

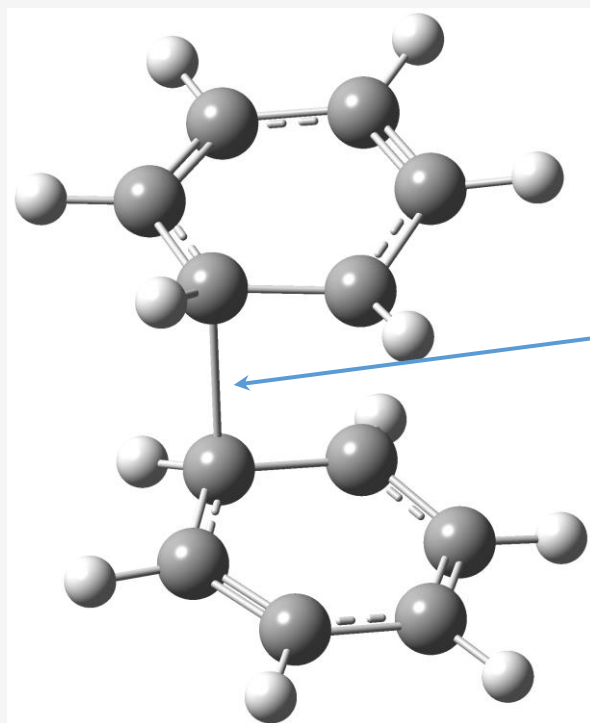
# The case of benzene monomer and dimer

## Conical intersection in benzene dimer:

### B. Dimer deformation

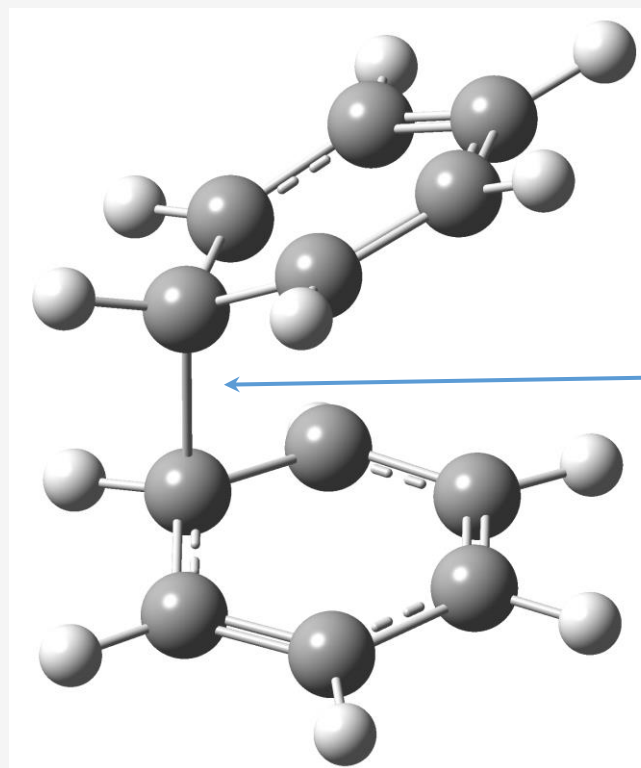
Method: SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP

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



$\approx 1.75 \text{ \AA}$   
 $\alpha = 60^\circ$

$\Delta E_{\text{Conf}} = +6.98 \text{ kcal/mol}$



$\tau(C - C - C' - C')$   
Dihedral angle

$\approx 1.59 \text{ \AA}$   
 $\alpha = 100^\circ$

$\Delta E_{\text{Conf}} = +7.54 \text{ kcal/mol}$

# The case of benzene monomer and dimer

---

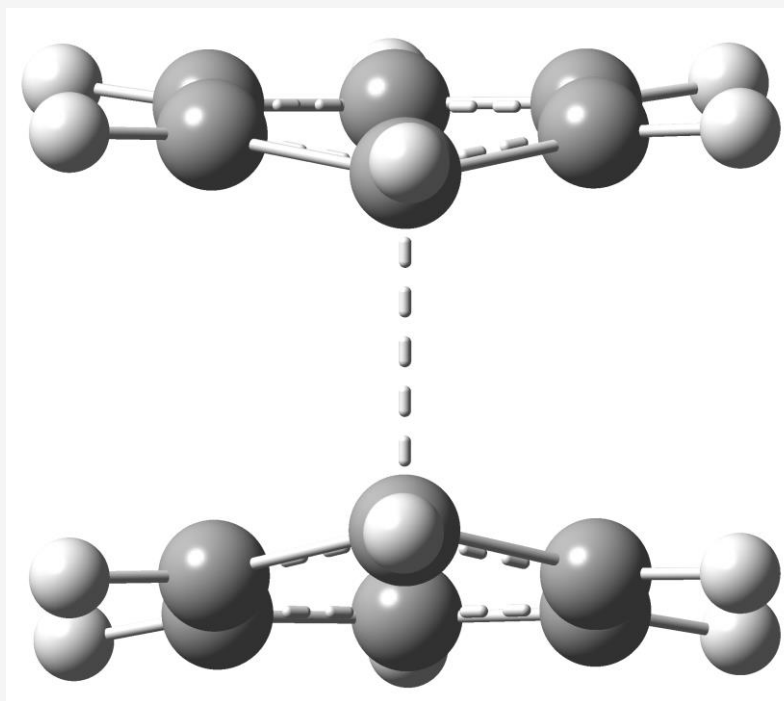
Conical intersection in benzene dimer:

Method: SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP

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

Results published in: [A. Bende, A.-A. Farcaş, \*Int. J. Mol. Sci.\* \*\*2023\*\*, \*24\*, 2906.](#)

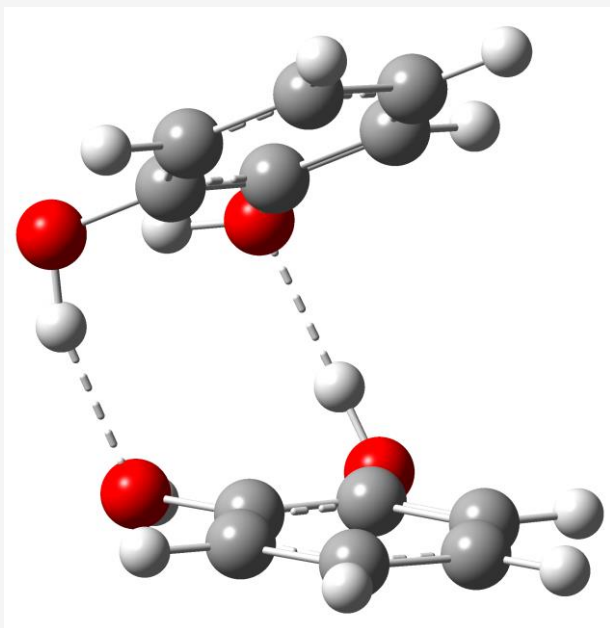
$$\Delta E_{TS} = +7.54 \text{ kcal/mol}$$





# The case of catechol dimer

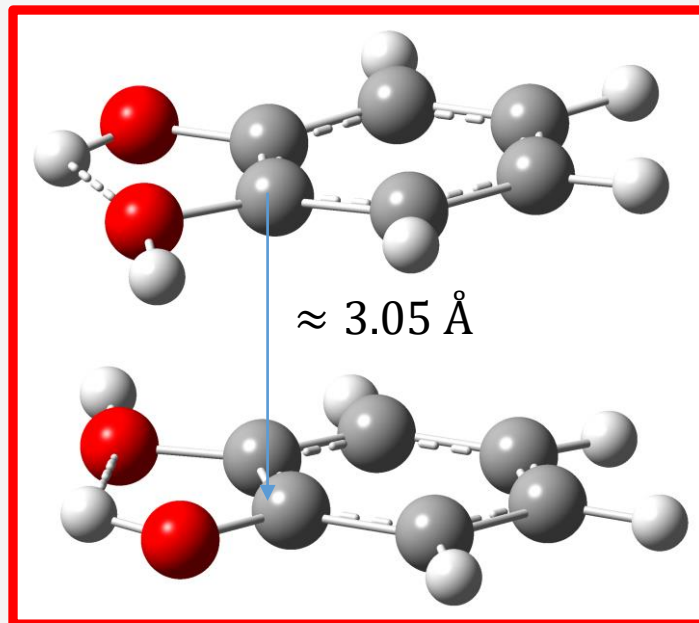
## Catechol dimer:



Ground state

$$\Delta E_{\text{Int}} = -5.21 \text{ kcal/mol}$$

## REF.



$S_1$  equilibrium geometry  
(excimer)

$$\Delta E_{\text{Int}} = -16.58 \text{ kcal/mol} \rightarrow \text{Strong hole – electron interaction}$$

$S_1$  (monomer): 4.75 eV

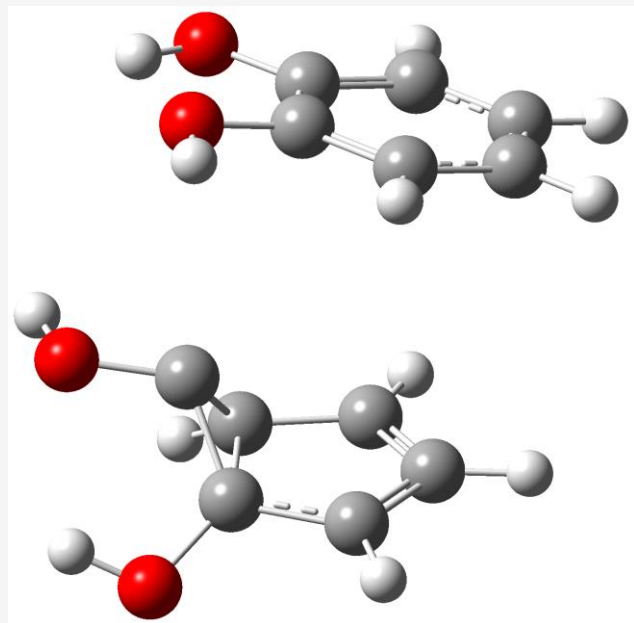
$S_1$  (dimer): 4.54 eV

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

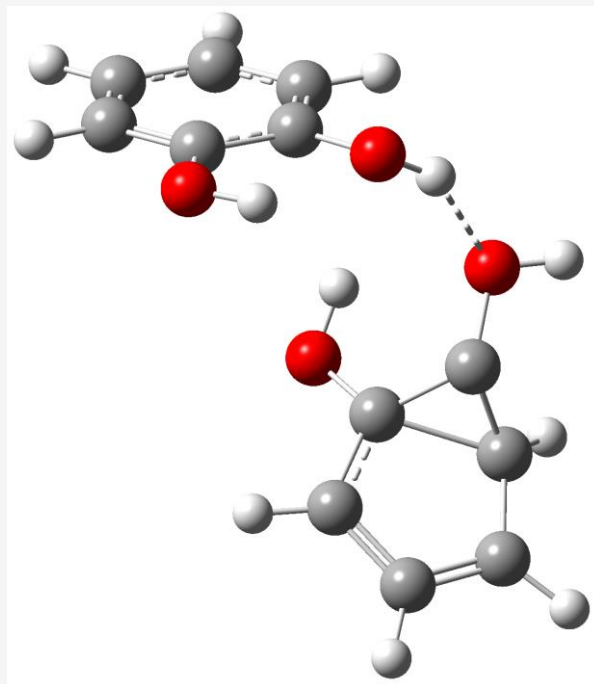
# The case of catechol dimer

Conical intersection in catechol dimer:

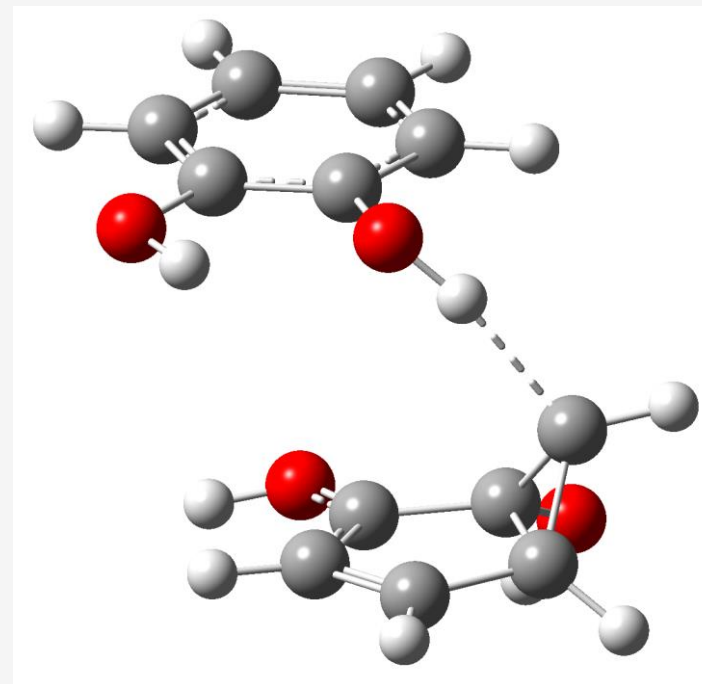
Method: SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP



$$\Delta E_{\text{Conf}} = +25.23 \text{ kcal/mol}$$



$$\Delta E_{\text{Conf}} = +24.66 \text{ kcal/mol}$$



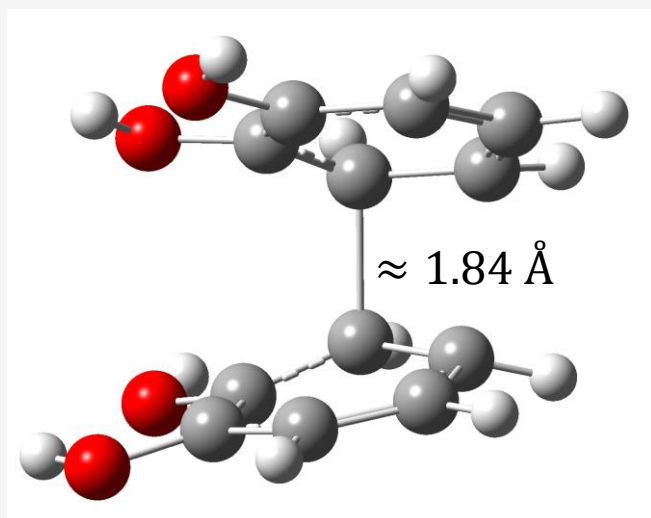
$$\Delta E_{\text{Conf}} = +21.14 \text{ kcal/mol}$$

Results published in: [A. Bende, A.A. Farçaş, A. Falamaş, A. Petran, Phys. Chem. Chem. Phys., 2022, 24, 29165.](#)

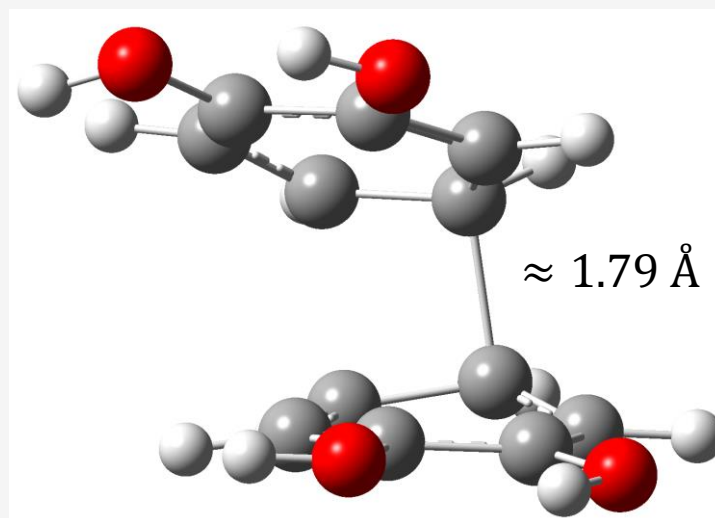
# The case of catechol dimer

Conical intersection in catechol dimer:

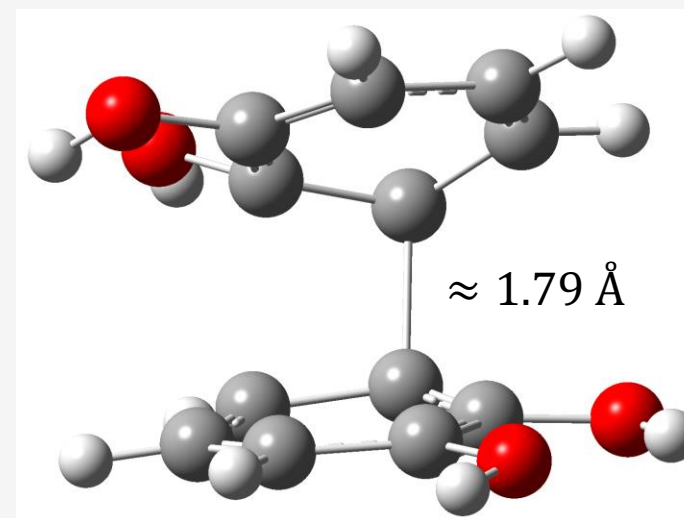
Method: SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP



$$\Delta E_{\text{Conf}} = +10.66 \text{ kcal/mol}$$



$$\Delta E_{\text{Conf}} = +11.20 \text{ kcal/mol}$$



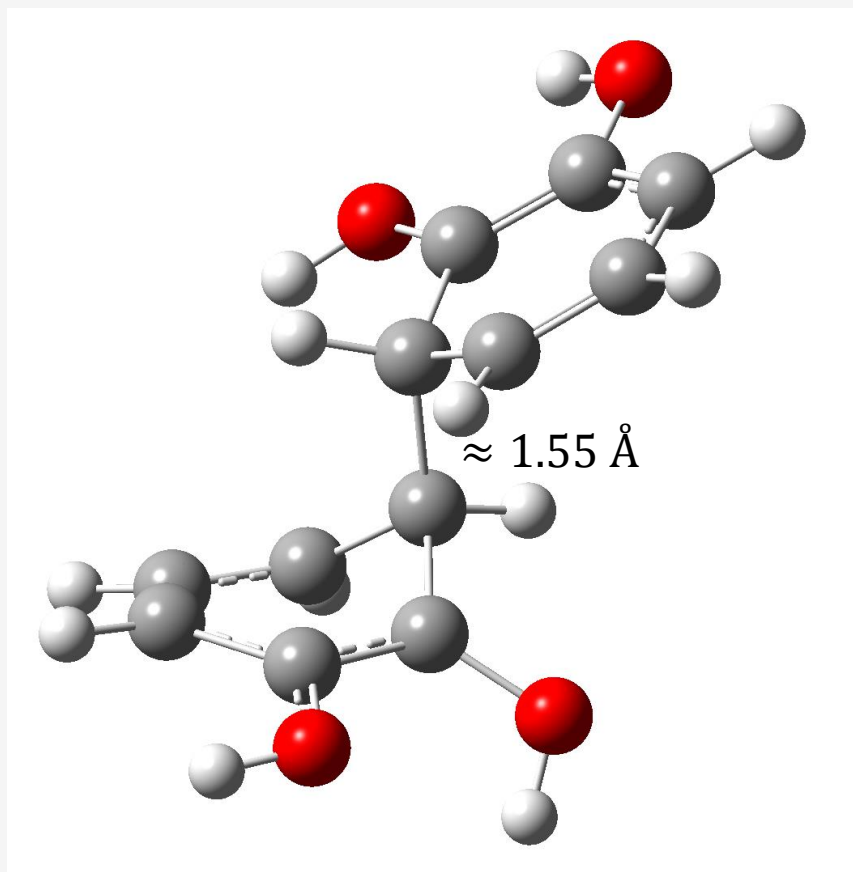
$$\Delta E_{\text{Conf}} = +7.39 \text{ kcal/mol}$$

# The case of catechol dimer

---

Conical intersection in catechol dimer:

Method: SF-TDDF/ $\omega$ B97X-D3/ma-def2-TZVPP



$$\Delta E_{\text{Conf}} = +13.08 \text{ kcal/mol}$$

Results published in: [A. Bende, A.A. Farçaş, A. Falamaş, 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;

# Acknowledgements:

- Founding: **PN-III-P4-ID-PCE-2020-0770**
- Research Team: **Dr. Alex-Adrian FARCAȘ, Dr. Alexandra FALAMAȘ and Dr. Anca PETRAN;**
- Data Center of INCDTIM; ORCA program developers

Thank You for Your Attention