Theoretical Study on Photophysical Properties of a Coumarin Derivative

Presenter: Dominika Tabor

Supervisor: dr hab. Monika Srebro-Hooper, prof. UJ

Quantum Chemistry Group - Department of Theoretical Chemistry

Faculty of Chemistry - Jagiellonian University in Kraków

Coumarins – characteristics

Properties and applications

Dual fluorescence and room-temperature phosphorescence phenomena

Examined system

Goals

Obtained results

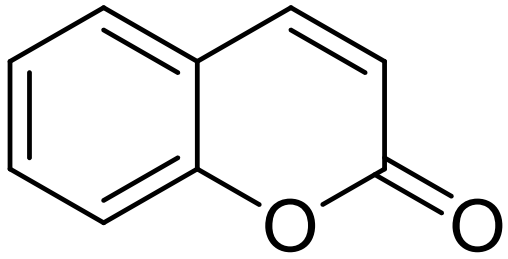
Conclusions and future plans

Coumarins

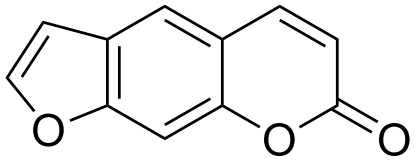
- class of heterocyclic, phenolic compounds with benzene and an alpha-pyrone ring

Natural coumarins can be divided into six groups:

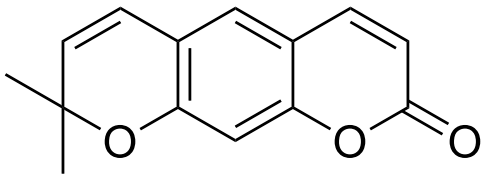
- simple coumarins
- furanocoumarins (linear type and angular type)
- pyranocoumarins (linear type and angular type)
- dihydrofurano coumarins
- phenyl coumarins
- bicoumarins



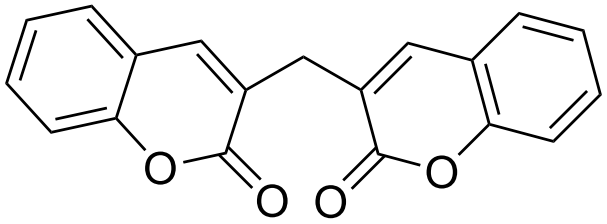
2H-chromen-2-one
coumarin



psolaren
furanocoumarin (linear)

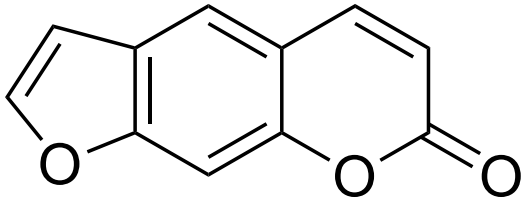


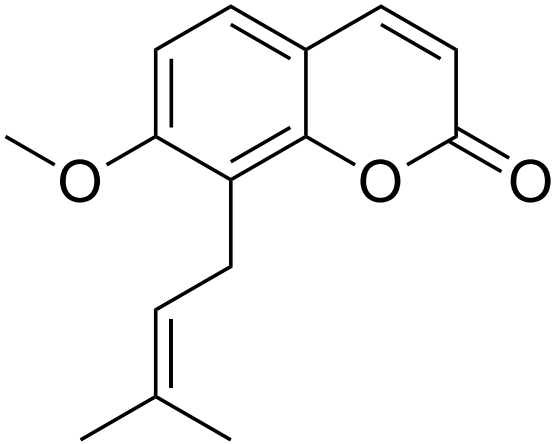
xanthyletin
pyranocoumarin (linear)

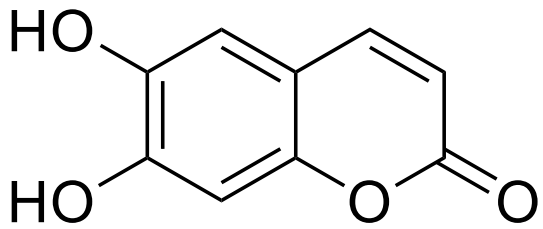


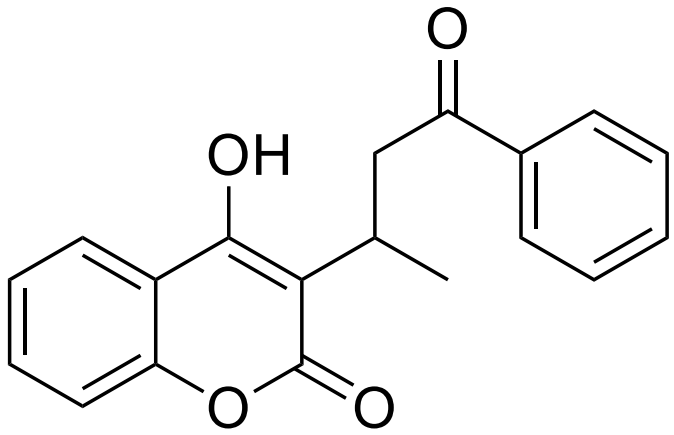
3,3'-methylenebis(2H-chromen-2-one)
bicoumarin

- photosensitizers
- enzyme inhibitors
- antiinflammatory agents
- anticoagulants
- antioxydants





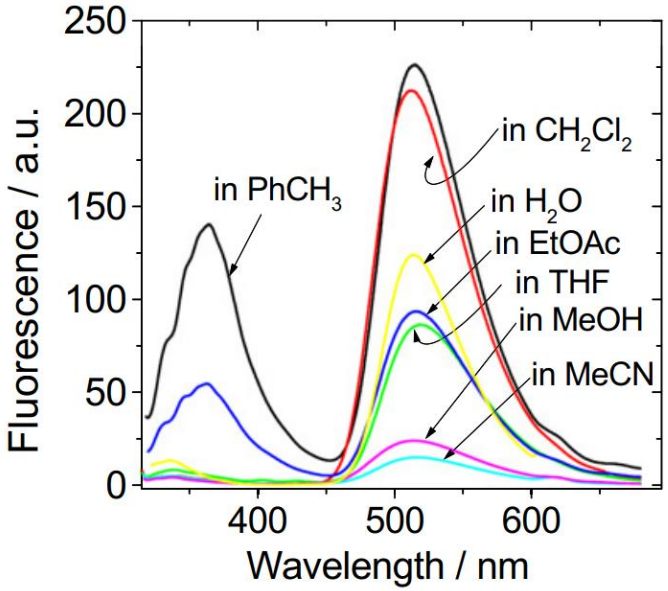


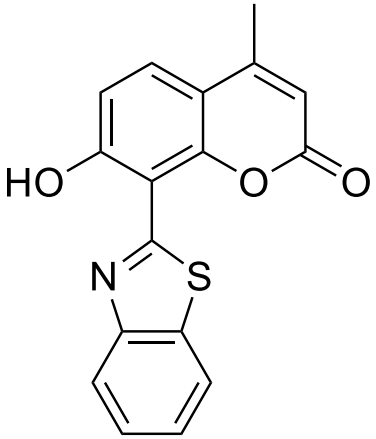


- photostability
- high quantum yield
- possibility of tuning properties through structural modifications

Dual fluorescence

- co-existence of multiple emissive states in different electronic and/or molecular structures
- breaching the Kasha's rule
- aggregation effects

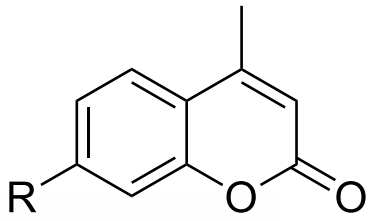




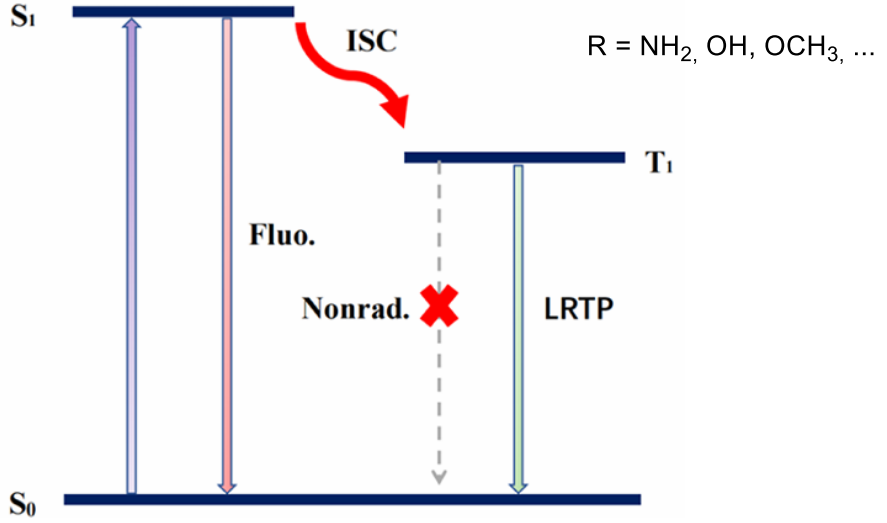
Lijuan Xie et al.
Dyes Pigm. **2012**, *92* (3), 1361-1369

Room-temperature phosphorescence

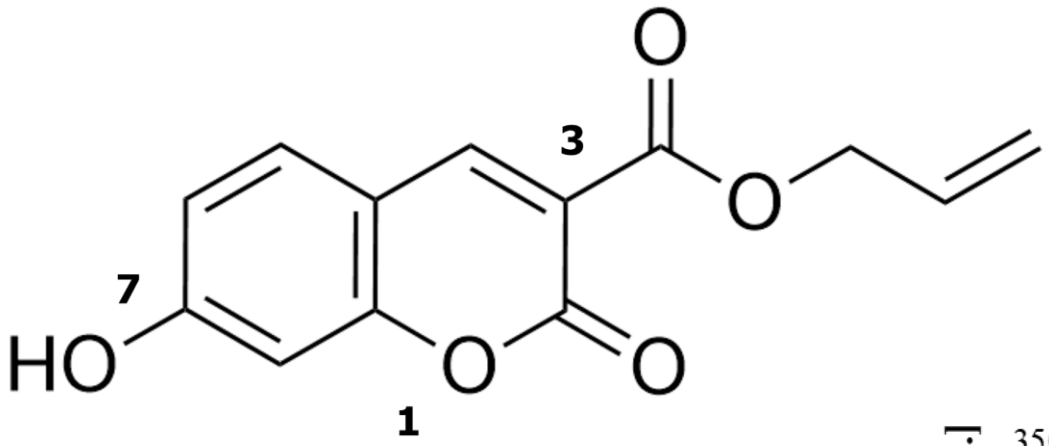
- promotion of intersystem crossing (ISC)
- reduction of non-radiative relaxation processes

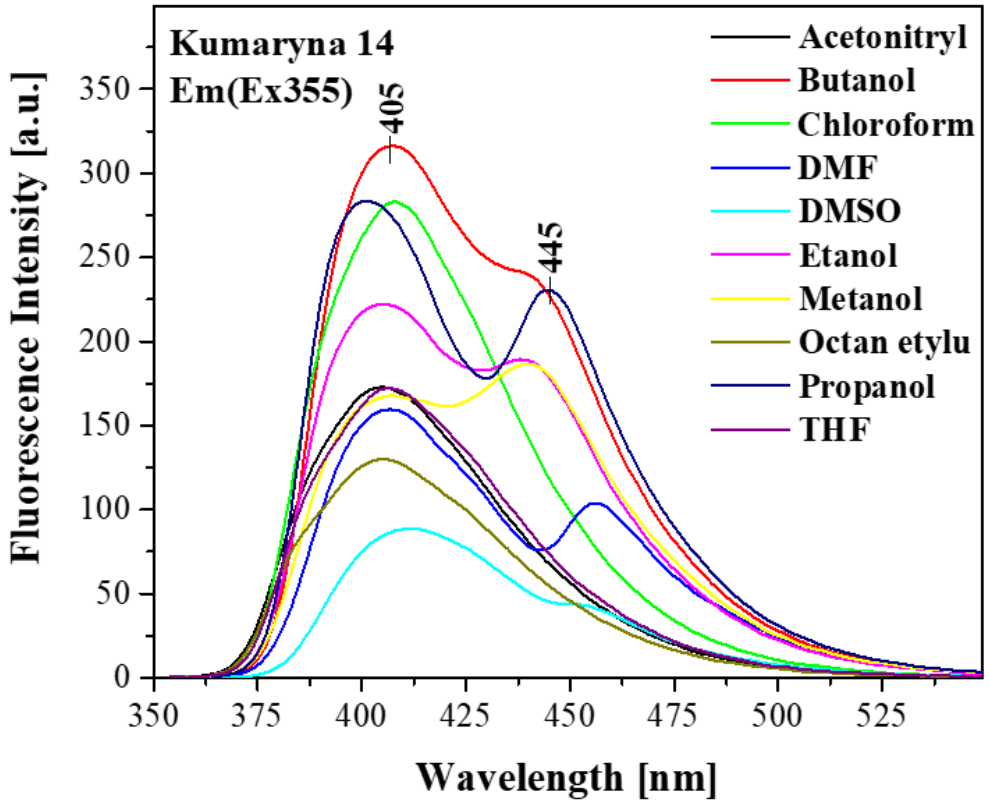


R = NH_2, OH, OCH_3, ...



Runcong Feng et al.
ACS Appl. Mater. Interfaces **2023**, *15* (25), 30717−30726

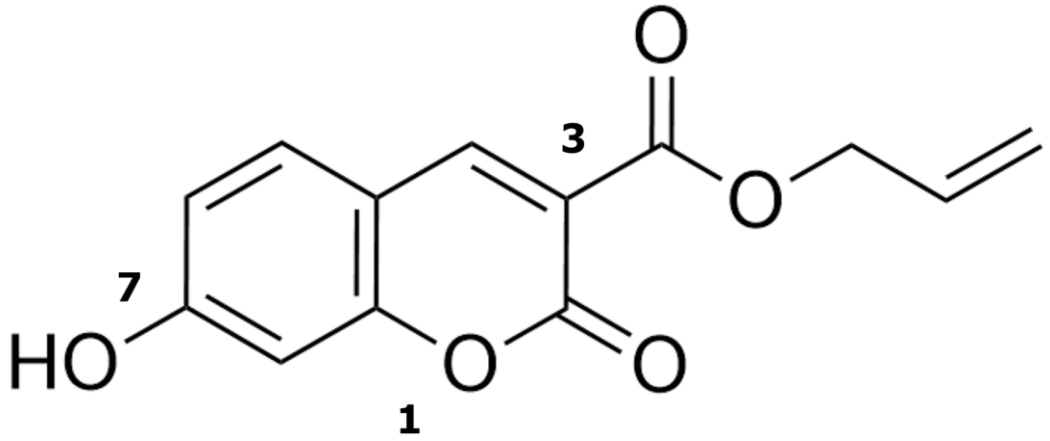




Prof. A. Matwijczuk, University of Life Sciences in Lublin

Development of a reliable theoretical model to explain observed emission properties of the system:

1. Conformational analysis
2. Modelling of emission properties (through optimization of S_1 and T_1 excited states)
3. Investigation of ISC (through calculation of spin-orbit coupling (SOC) interactions between S_1 and low-energy triplet excited states)



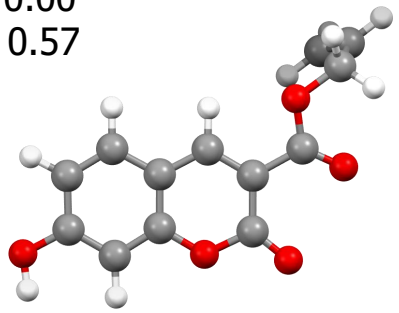
Conformational analysis

Program: conformer-rotamer sampling tool CREST

Philip Pracht et al.
J. Chem. Phys., **2024**, 160, 114110

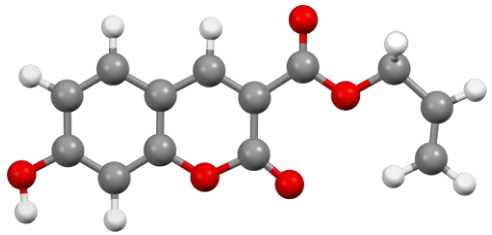
Program: Gaussian 16
Method: DFT
Functional: B3LYP
Basis set: 6-311++G(d,p)
Environment: PCM (methanol, ε = 32.6)

ΔE = 0.00
ΔG = 0.57



N_B = 18.01%

ΔE = 0.19
ΔG = 0.22



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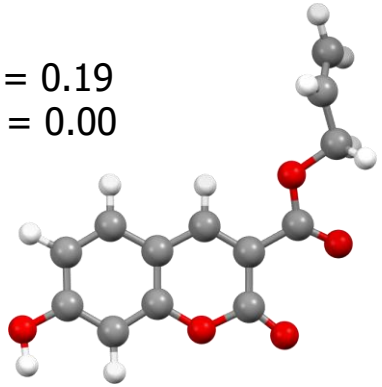

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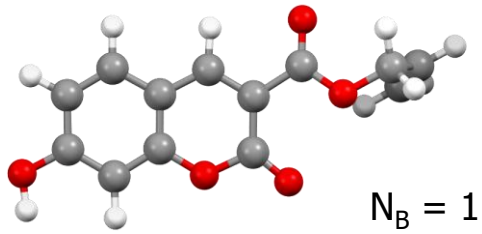

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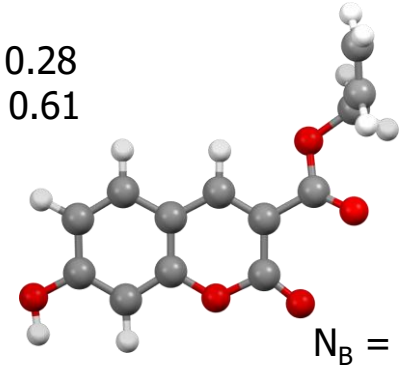

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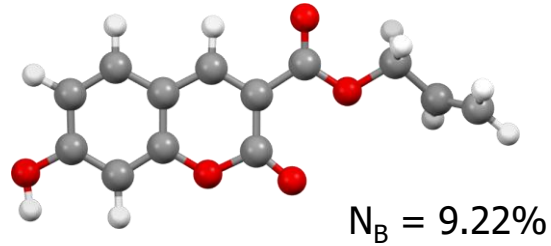

N_B = 9.22%

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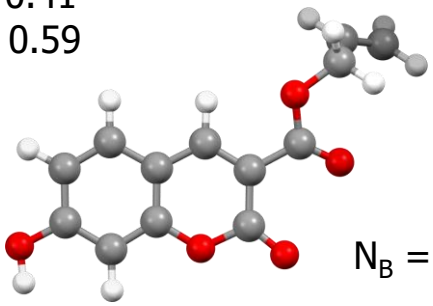

N_B = 9.03%

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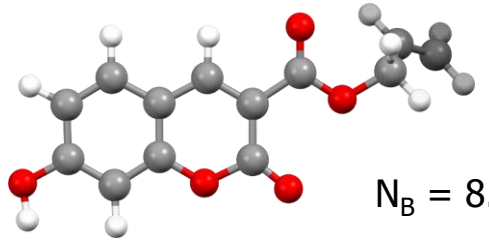

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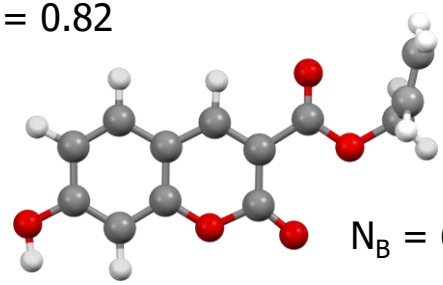

N_B = 6.26%

ΔE / kcal·mol^{-1} N_B – Boltzmann populations at 298 K based on E
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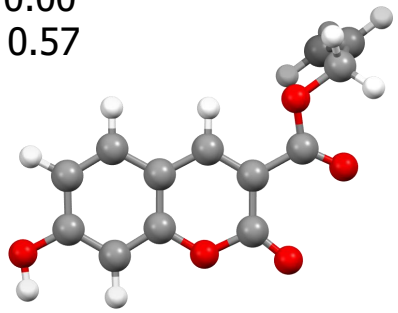

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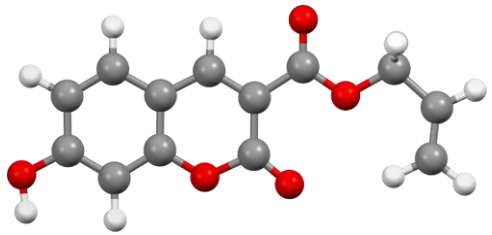

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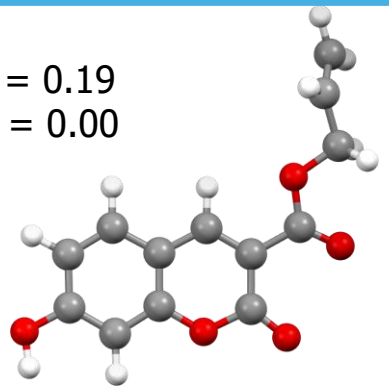

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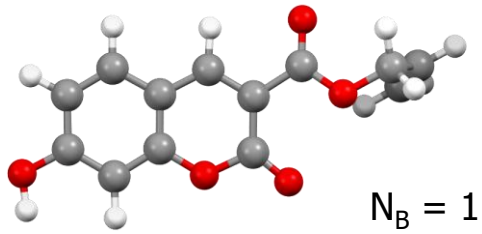

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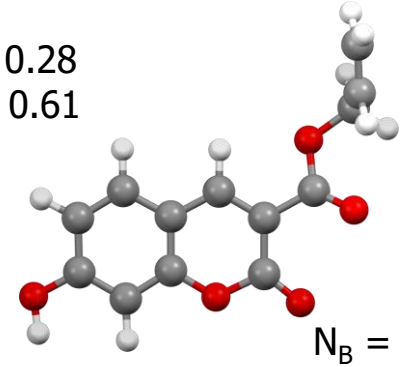

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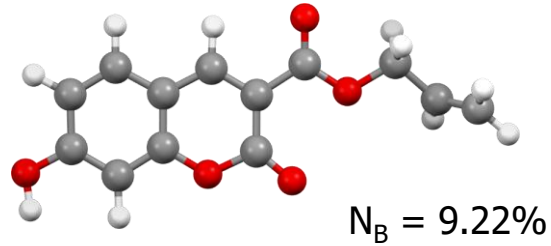

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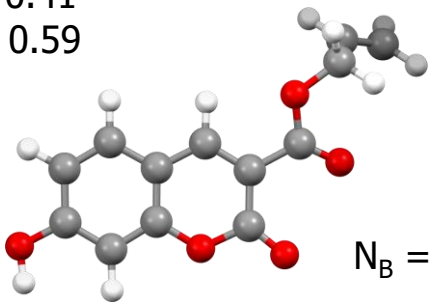

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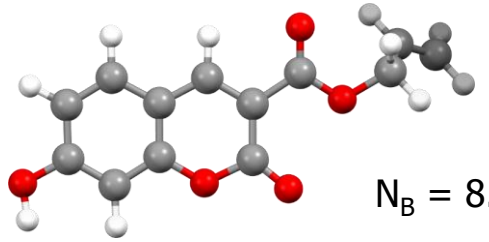

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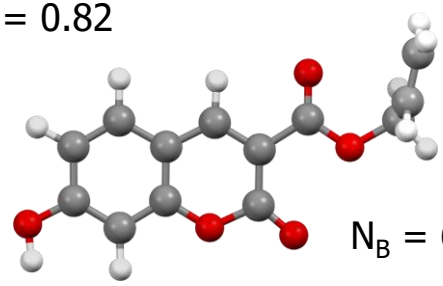

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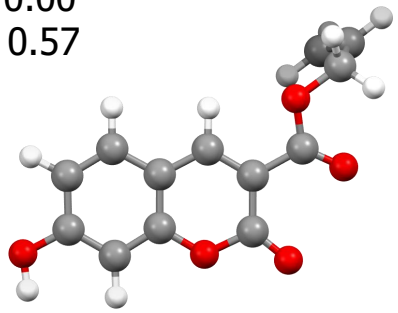

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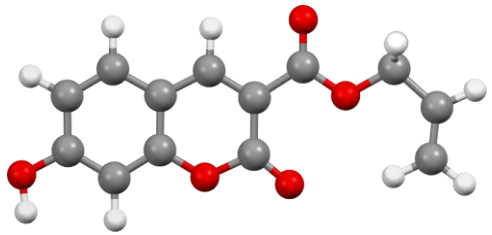

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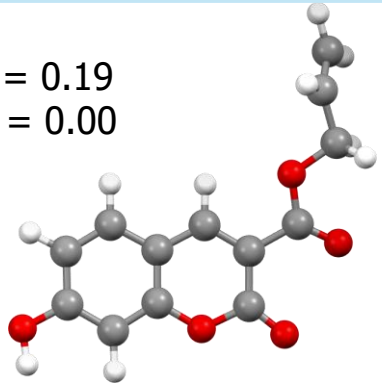

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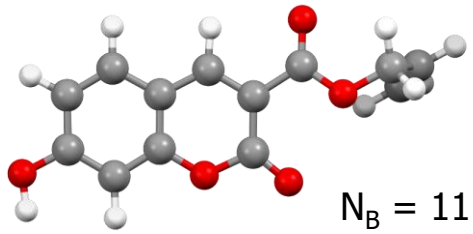

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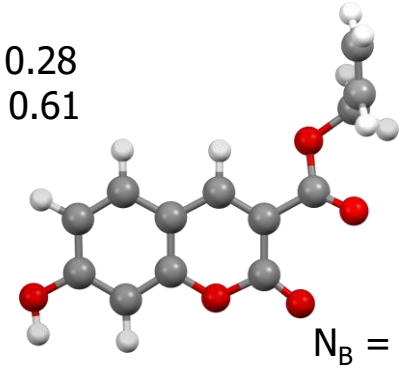

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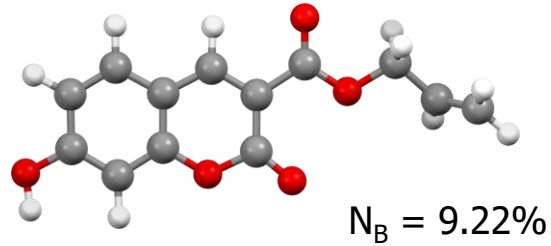

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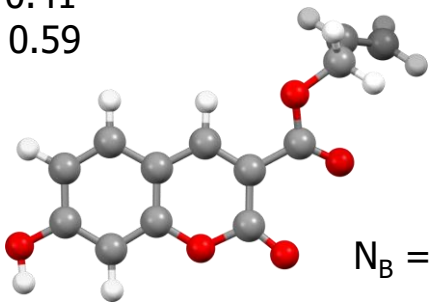

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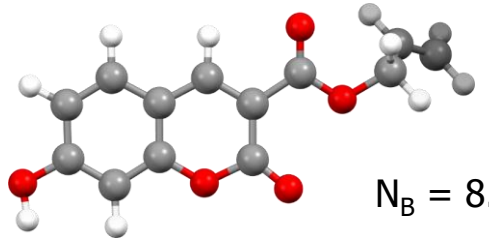

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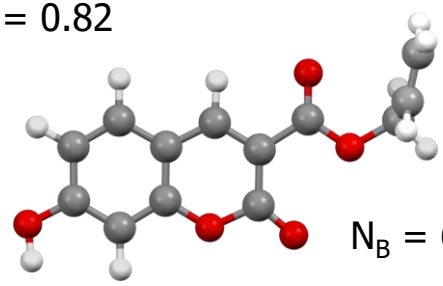

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ΔE / kcal·mol^{-1} N_B – Boltzmann populations at 298 K based on E
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DFT B3LYP//6-311++G(d,p)

Choice of functionals for TD-DFT calculations

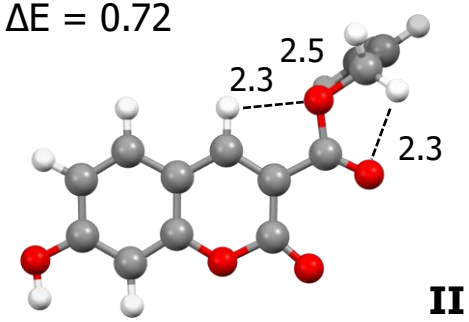
Program: DELFI by D. Avagliano

Davide Avagliano et al.
Chem. Sci., **2024**, 15, 4489-4503

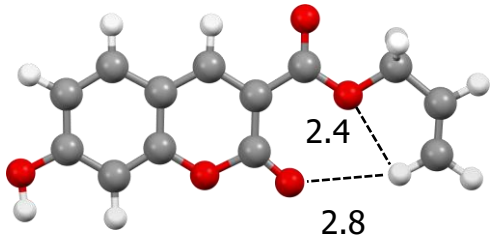
S_1 optimization

Program: Gaussian 16/ORCA
Method: TD-DFT, CCSD
Functional: B3LYP, CAM-B3LYP, ωB97X-D, LC-ωPBEh, ωB97-XV, rCAM-B3LYP, TPSSh, M06, M062X, M11
Basis set: 6-311++G(d,p)
Environment: PCM (methanol, ε = 32.6)

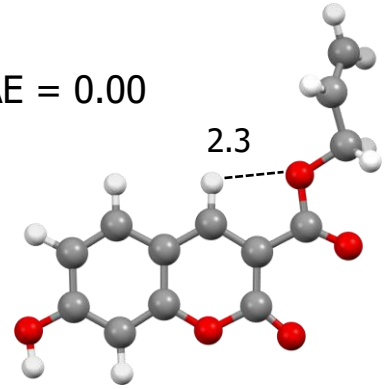
I ΔE = 0.72



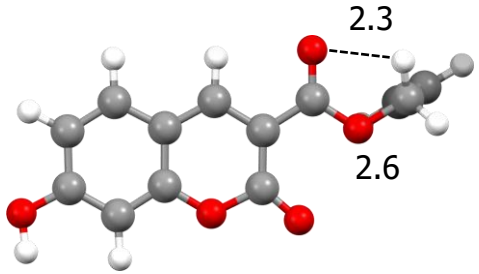
II ΔE = 0.32



III ΔE = 0.00

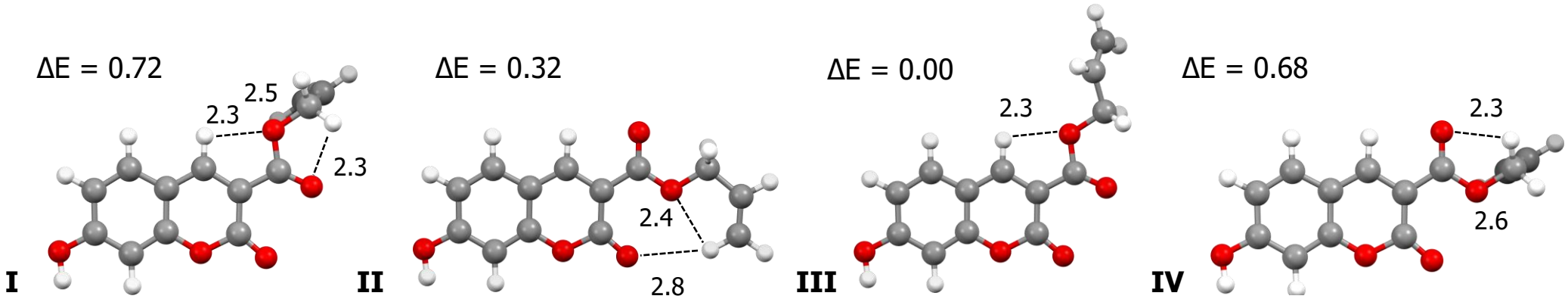


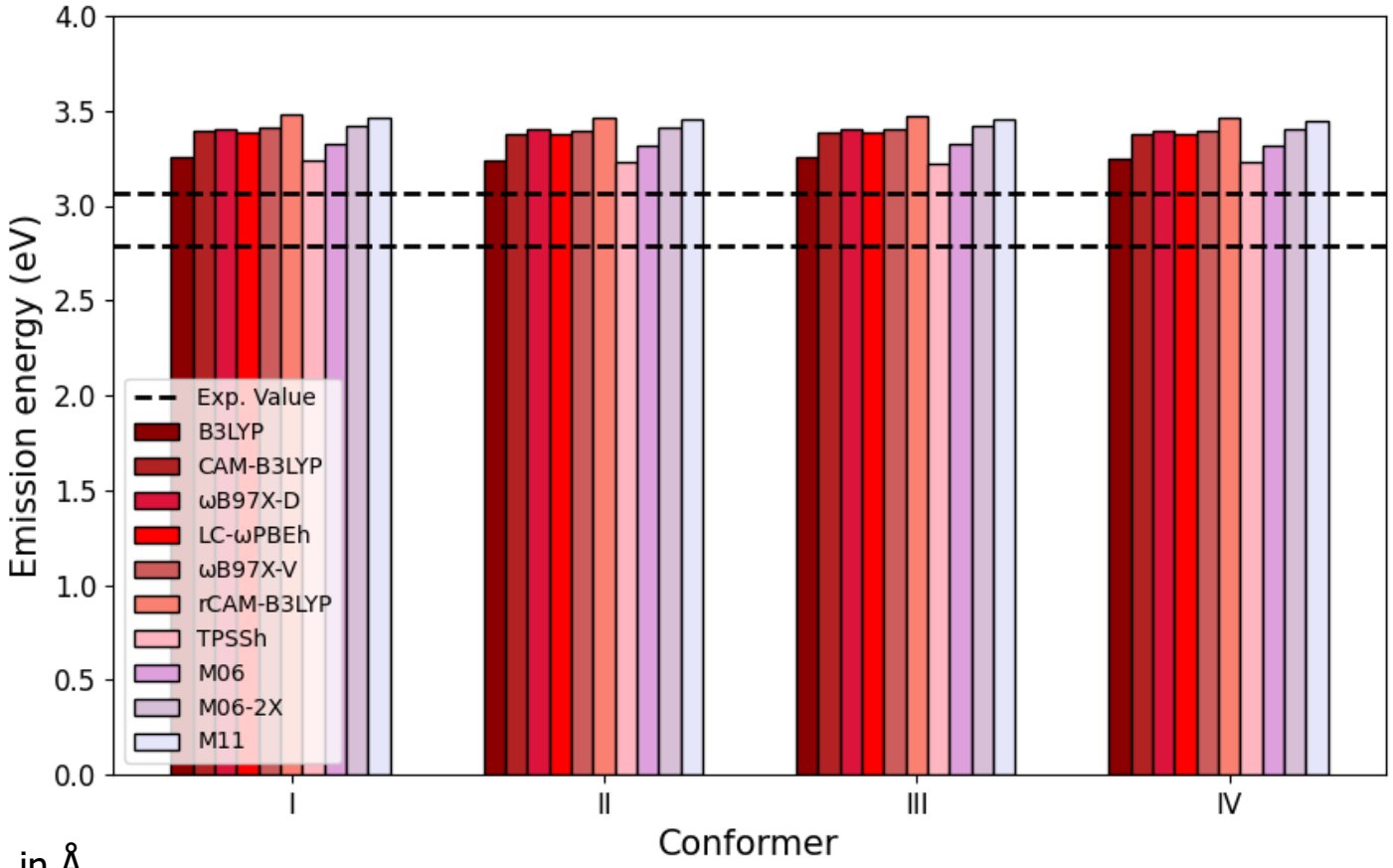
IV ΔE = 0.68



ΔE / kcal·mol^{-1} dist. in Å

TD-DFT TPSSh//6-311++G(d,p)



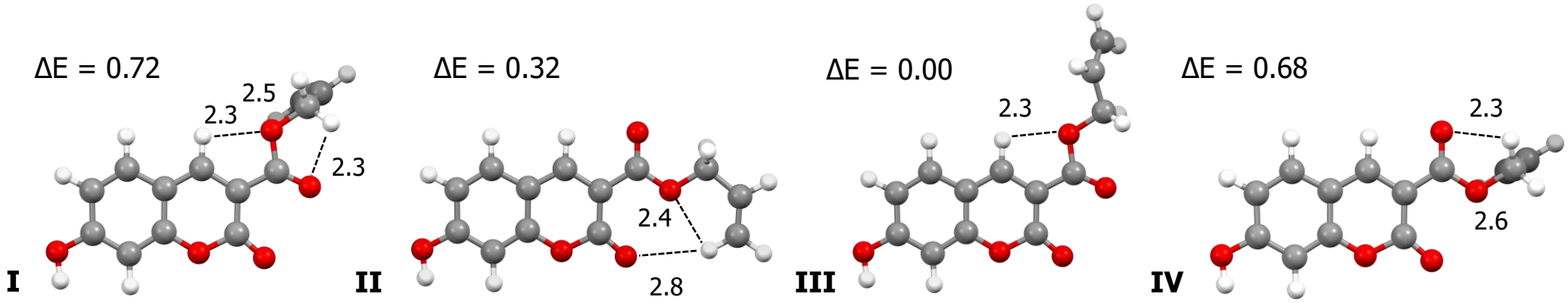


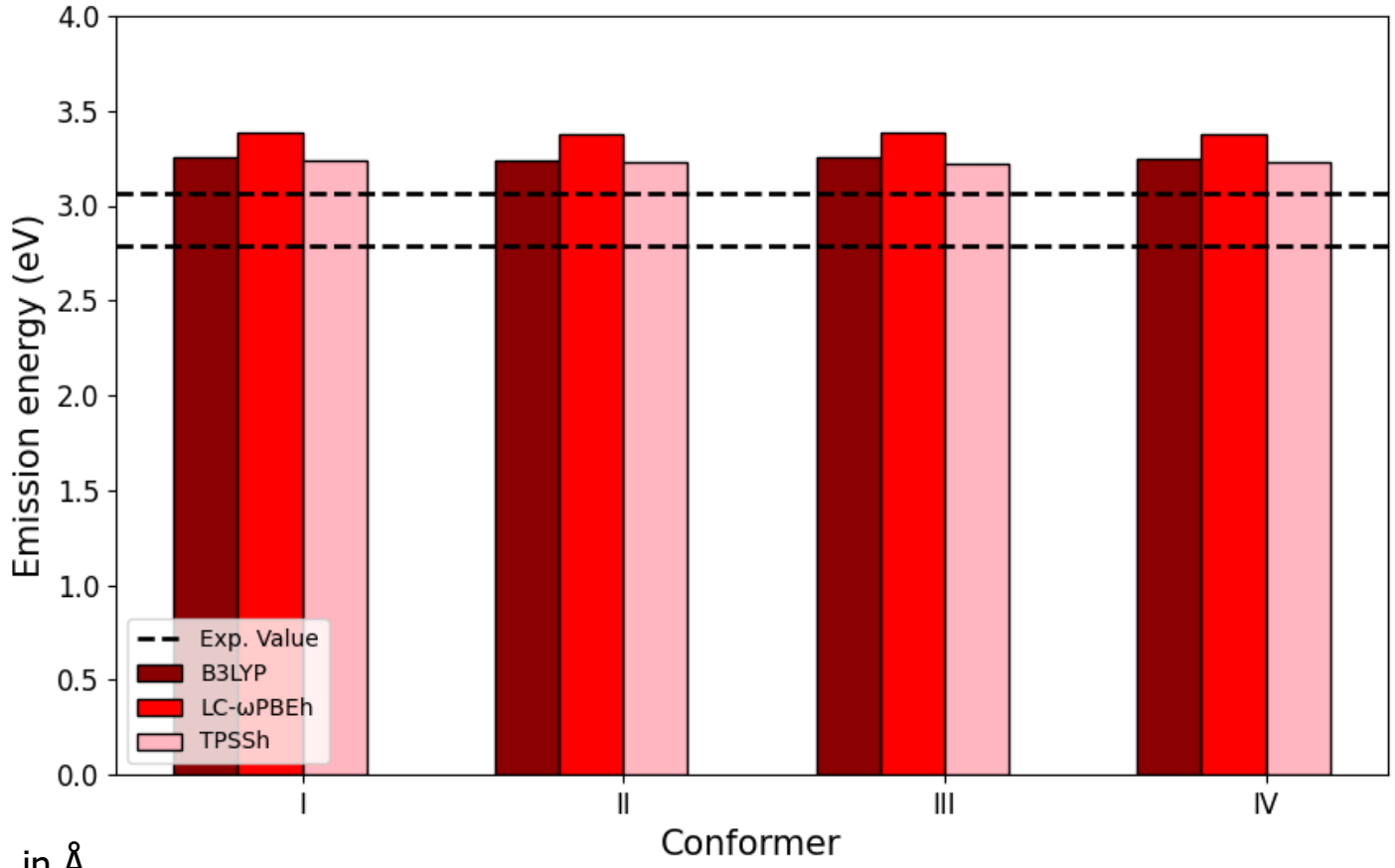
high-energy signal
E = 3.06 eV

low-energy signal
E = 2.79 eV

ΔE / kcal·mol^{-1} dist. in Å

TD-DFT TPSSh//6-311++G(d,p)



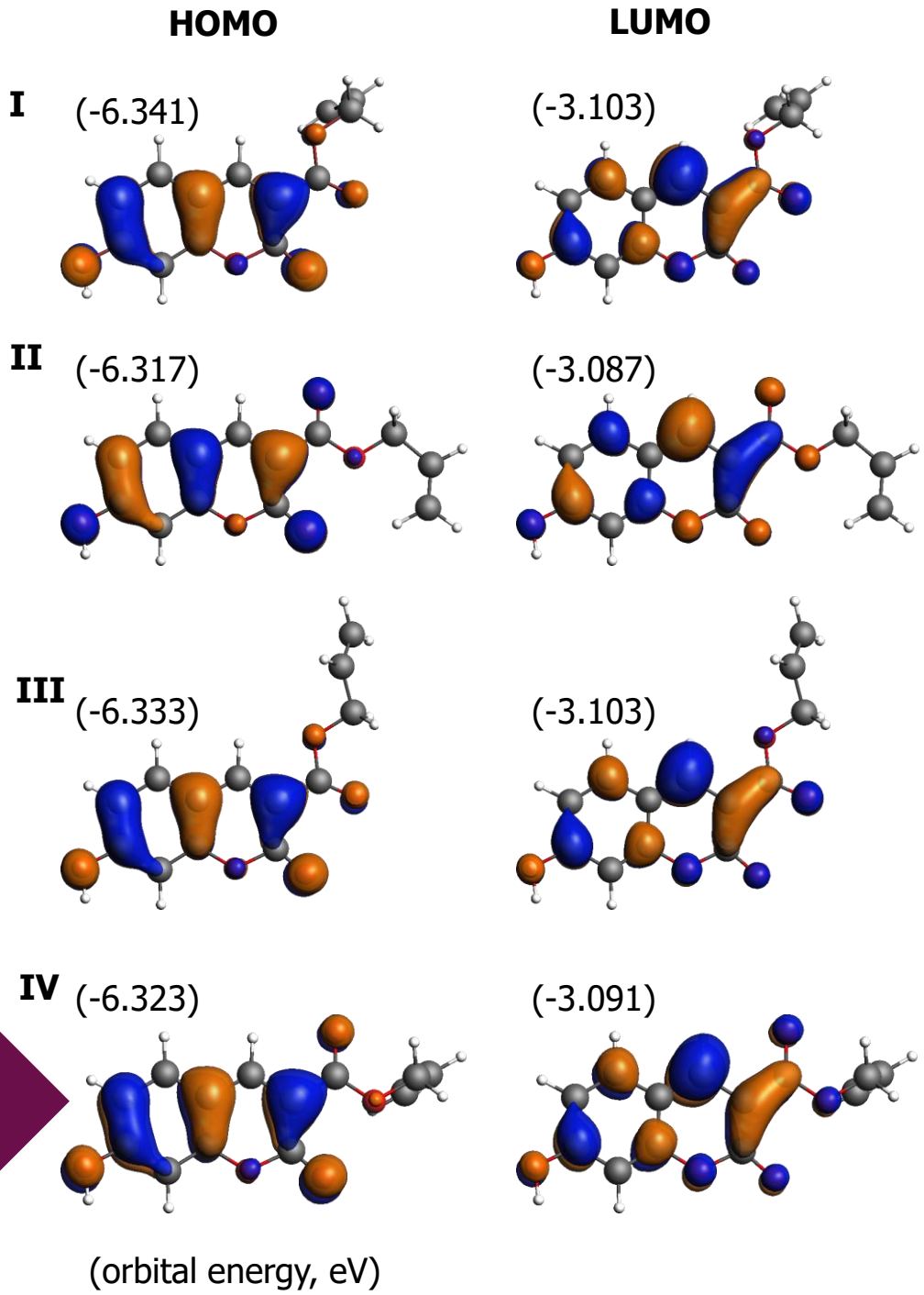


high-energy signal
E = 3.06 eV

low-energy signal
E = 2.79 eV

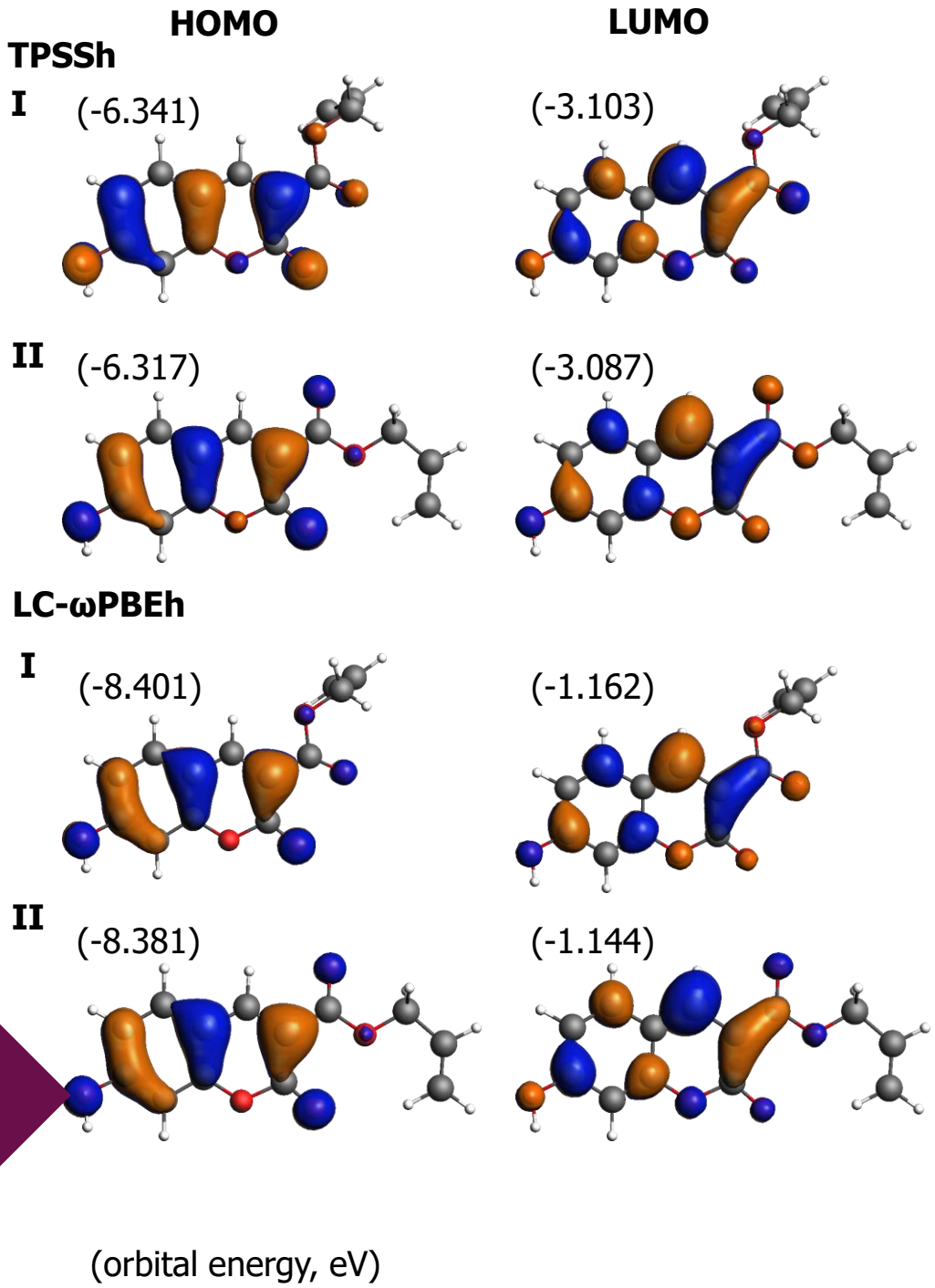
ΔE / kcal·mol^{-1} dist. in Å

TD-DFT TPSSh//6-311++G(d,p)



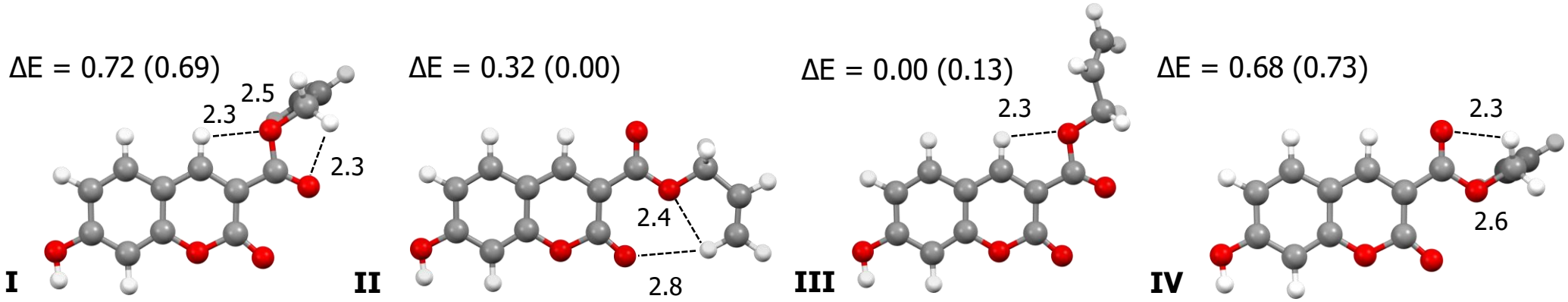
		E [eV] (λ [nm])	f	H ← L: %
exp.		3.061 (405)	–	–
exp.		2.786 (445)	–	–
TPSSh	**I**	3.234 (383)	0.700	97.3
	II	3.226 (384)	0.715	97.7
	III	3.219 (385)	0.686	95.6
	IV	3.227 (384)	0.704	97.7

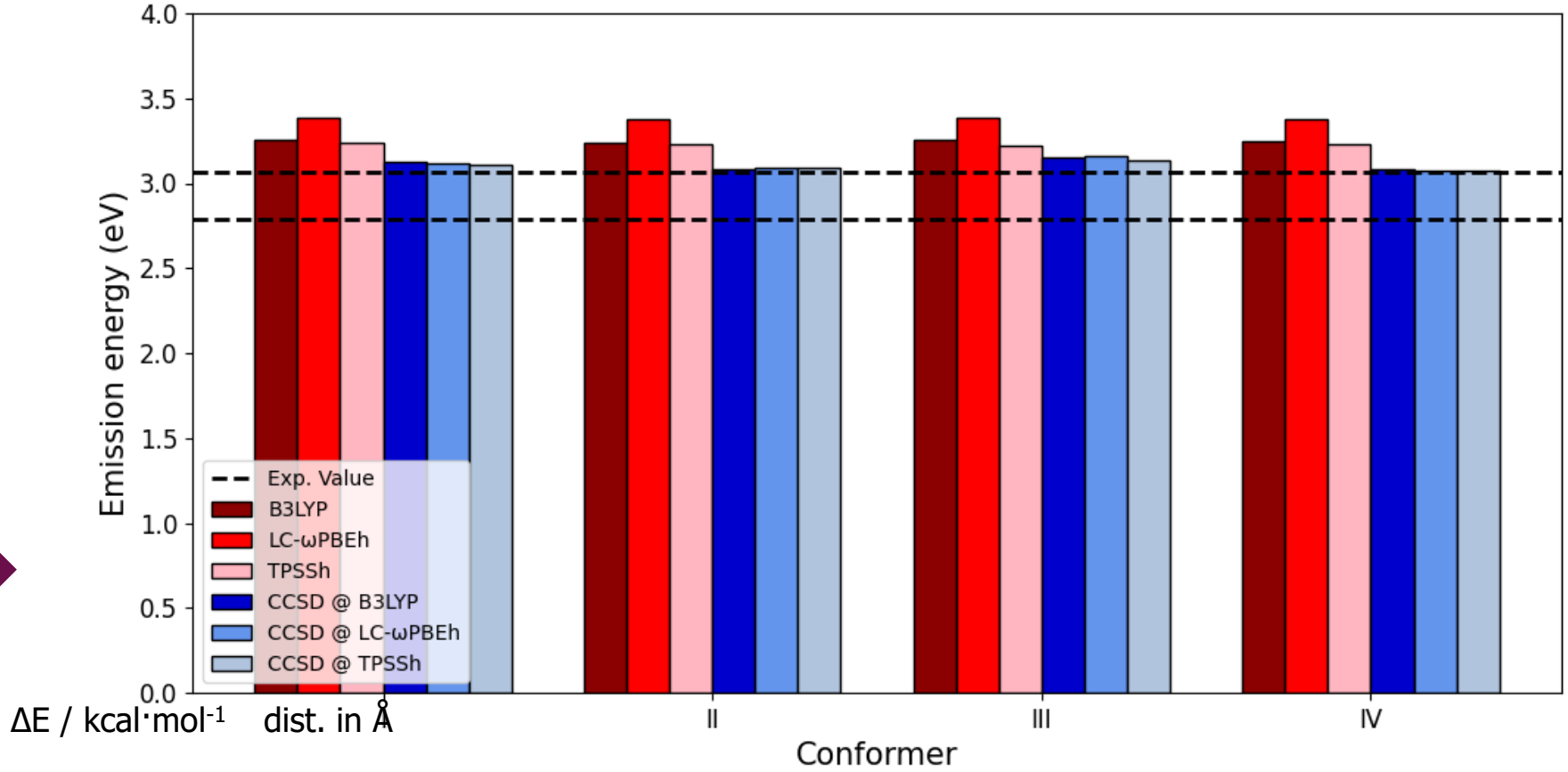
TD-DFT TPSSh//6-311++G(d,p)



		E [eV] (λ [nm])	f	H ← L: %
	exp.	3.061 (405)	–	–
	exp.	2.786 (445)	–	–
B3LYP	**I**	3.257 (381)	0.786	98.1
	II	3.241 (383)	0.785	98.2
	III	3.253 (381)	0.791	98.1
	IV	3.243 (382)	0.779	98.2
TPSSh	**I**	3.234 (383)	0.700	97.3
	II	3.226 (384)	0.715	97.7
	III	3.219 (385)	0.686	95.6
	IV	3.227 (384)	0.704	97.7
LC-ωPBEh	**I**	3.389 (366)	0.841	96.7
	II	3.379 (367)	0.833	96.8
	III	3.386 (366)	0.845	96.8
	IV	3.379 (367)	0.829	96.8

TD-DFT TPSSh (CCSD @ TPSSh)//6-311++G(d,p)



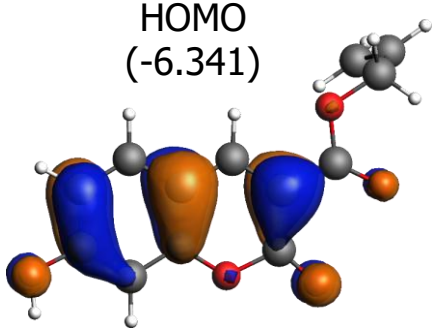


high-energy signal
E = 3.06 eV

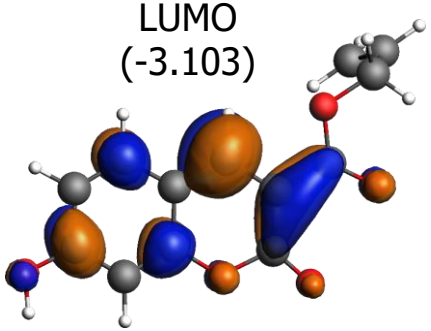
low-energy signal
E = 2.79 eV

TPSSh

HOMO (-6.341)

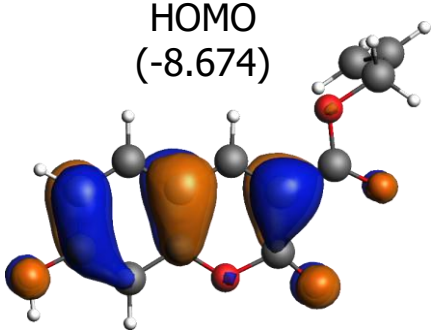


LUMO (-3.103)

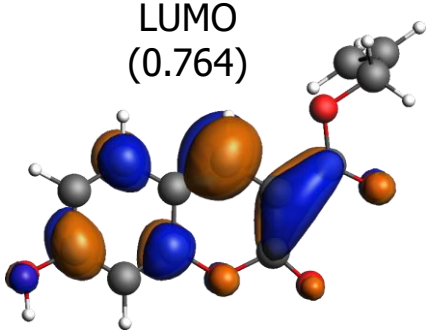


CCSD @ TPSSh

HOMO (-8.674)



LUMO (0.764)

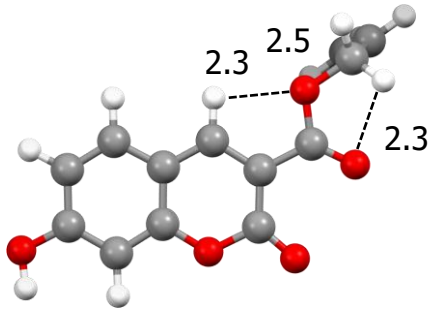


(orbital energy, eV)

	E [eV] (λ [nm])	f	H ← L: %
exp.	**3.061 (405)**	–	–
exp.	2.786 (445)	–	–
B3LYP	3.257 (381)	0.786	98.1
TPSSh	3.234 (383)	0.700	97.3
LC-ωPBEh	3.389 (366)	0.841	96.7
CCSD @ B3LYP	**3.125 (397)**	0.702	95.4
CCSD @ TPSSh	**3.110 (399)**	0.663	95.4
CCSD @ LC-ωPBEh	**3.114 (398)**	0.726	95.6

ΔE = 0.72 (0.69)

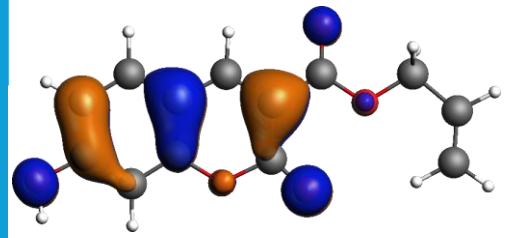
ΔE / kcal·mol^{-1} dist. in Å



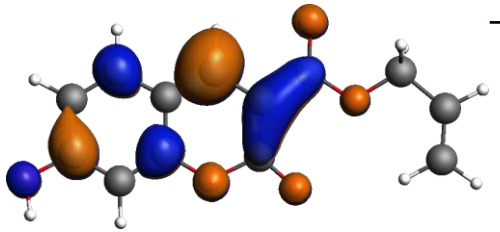
I

TPSSh

HOMO (-6.317)

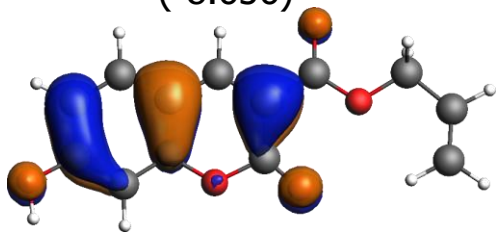


LUMO (-3.087)

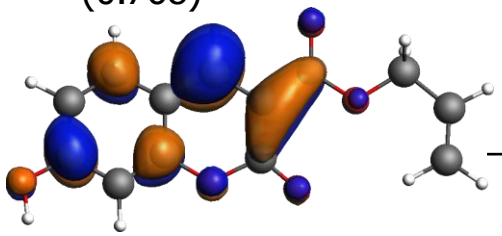


CCSD @ TPSSh

HOMO (-8.656)



LUMO (0.768)



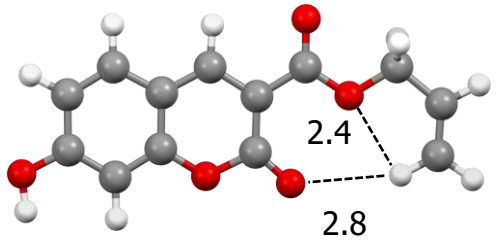
(orbital energy, eV)

	E [eV] (λ [nm])	f	H ← L: %
exp.	**3.061 (405)**	–	–
exp.	2.786 (445)	–	–
B3LYP	3.241 (383)	0.785	98.2
TPSSh	3.226 (384)	0.715	97.7
LC-ωPBEh	3.379 (367)	0.833	96.8
CCSD @ B3LYP	**3.081 (403)**	0.723	94.5
CCSD @ TPSSh	**3.087 (402)**	0.749	95.4
CCSD @ LC-ωPBEh	**3.090 (401)**	0.802	95.5

ΔE = 0.32 (0.00)

ΔE / kcal·mol^{-1} dist. in Å

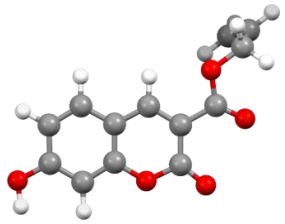
II

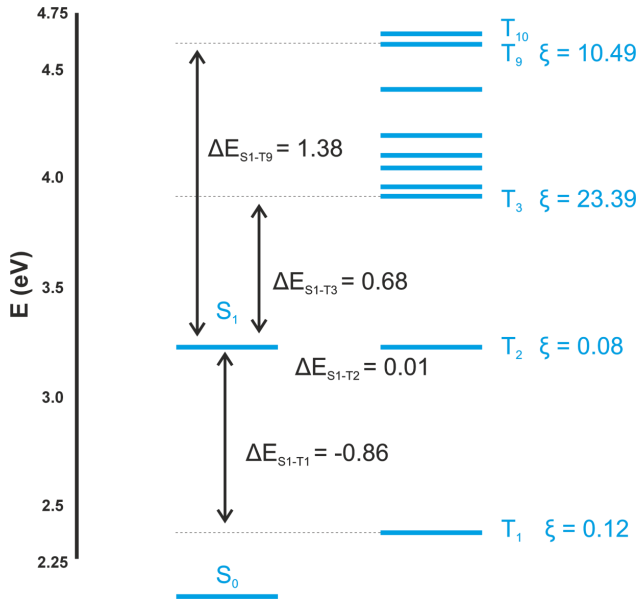


SOC calculations

Program: ADF
Method: TD-DFT
Functional: B3LYP
Basis set: TZ2P
Environment: COSMO (methanol, $\varepsilon = 32.6$)

I

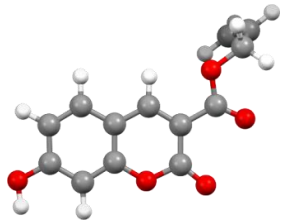


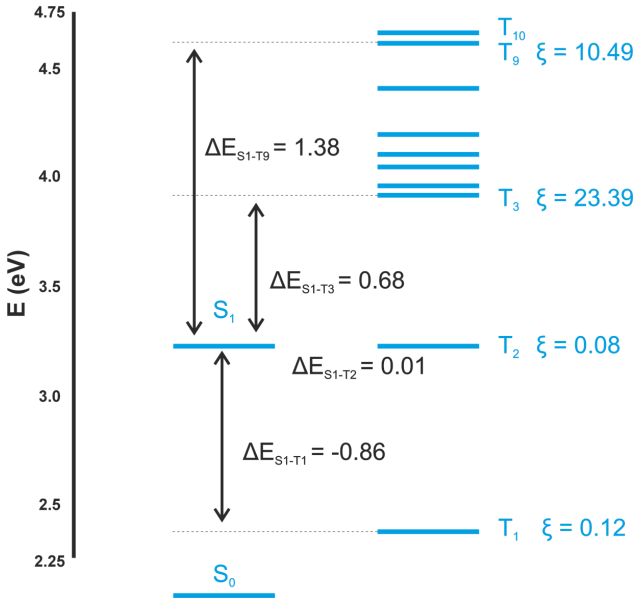


ξ / cm^{-1}
ΔE / eV

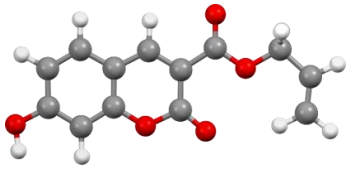
TD-DFT B3LYP//TZ2P @ B3LYP geometries

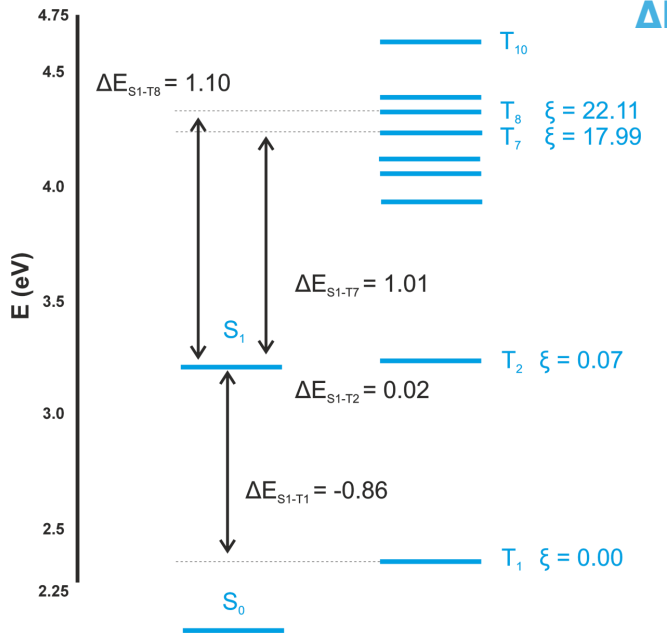
I



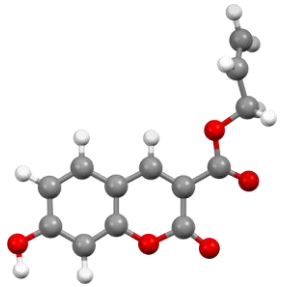


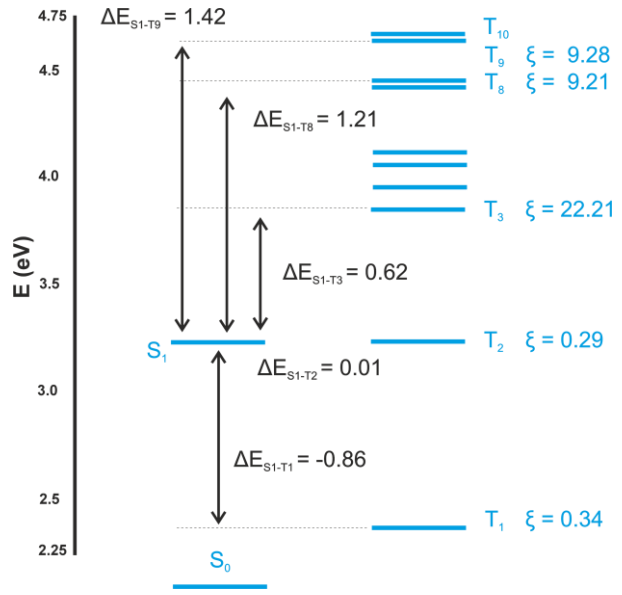
II



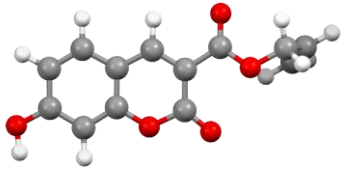


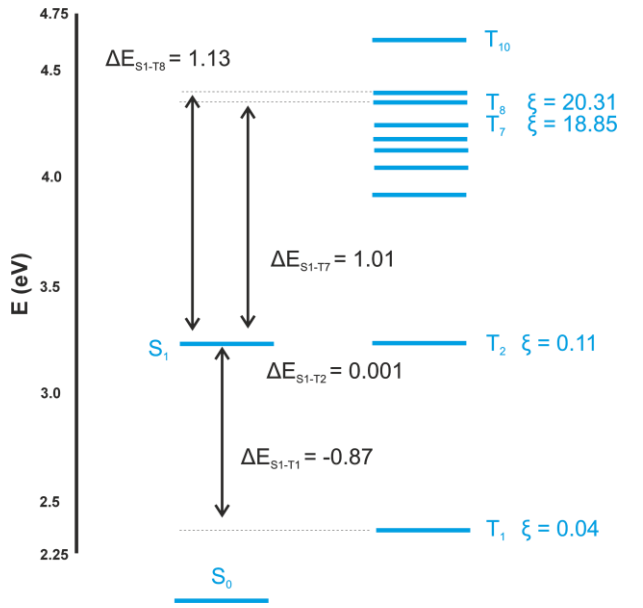
III





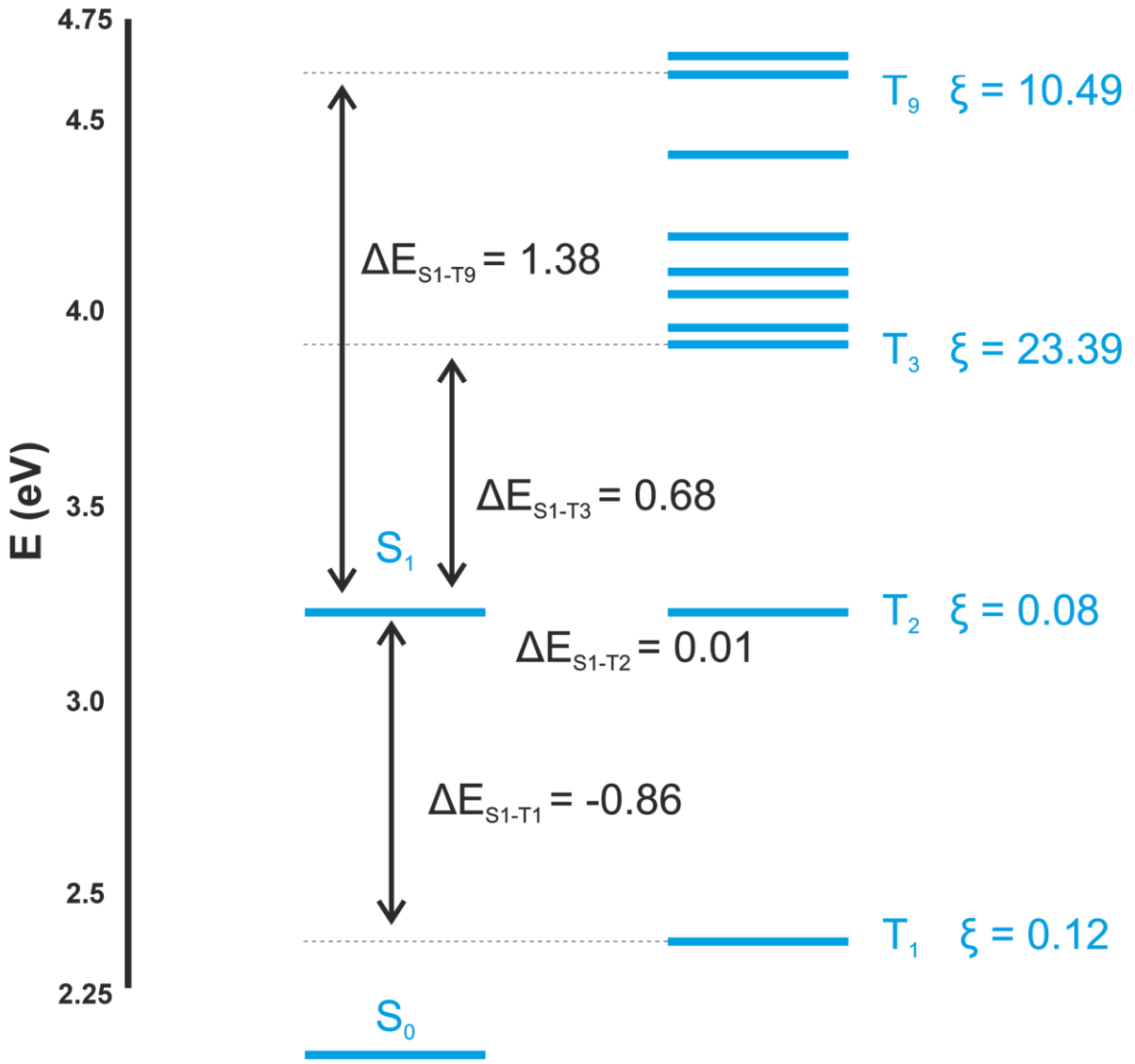
IV



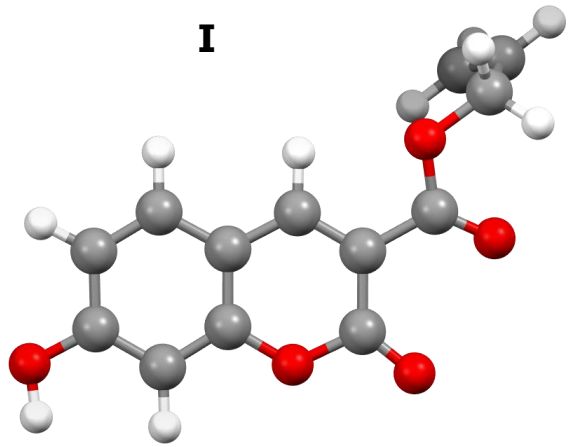


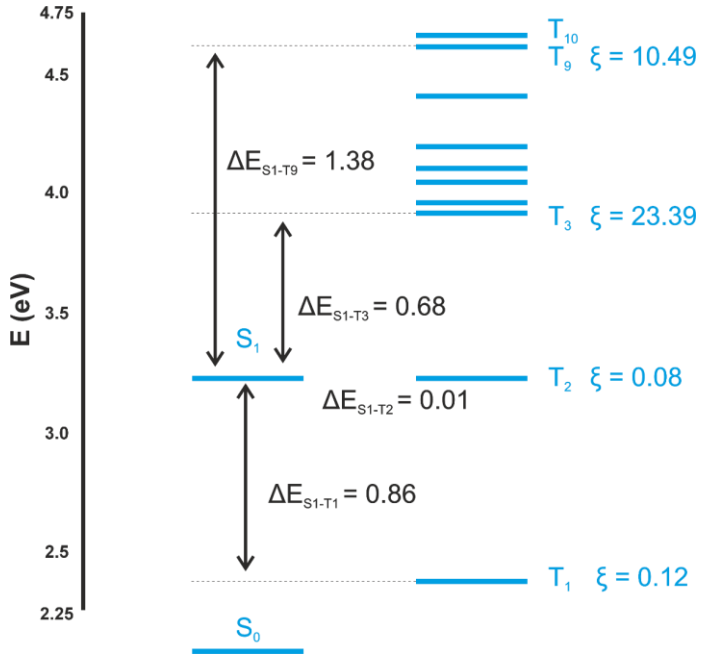
TD-DFT B3LYP//TZ2P @ B3LYP geometries

ξ / cm^{-1}
ΔE / eV



I

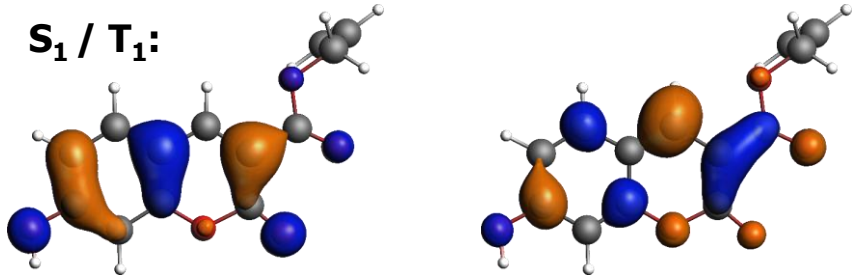




$^1(\pi, \pi^*) \rightarrow {}^3(n, \pi^*)$

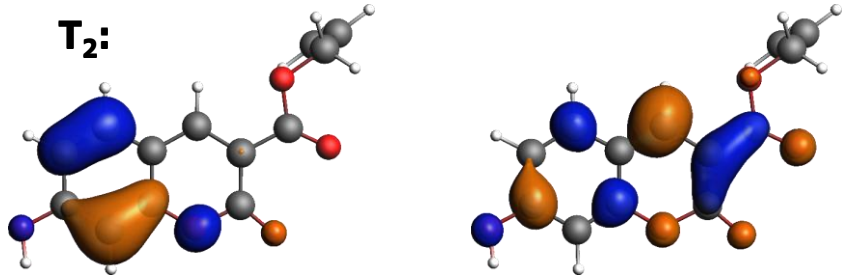
$^1(\pi, \pi^*) \rightarrow {}^3(\pi, \pi^*)$

S_1 / T_1:



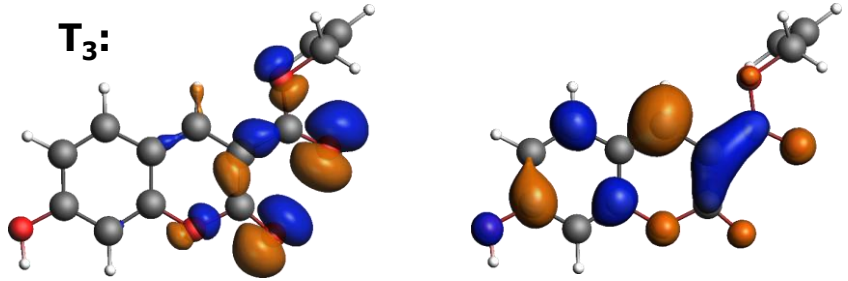
$\pi \rightarrow \pi^*$

T_2:



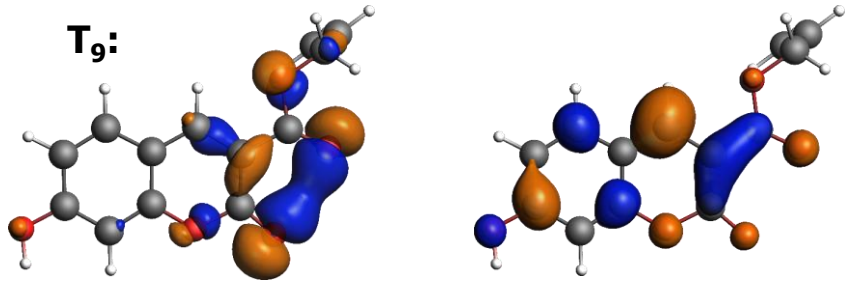
$\pi \rightarrow \pi^*$

T_3:



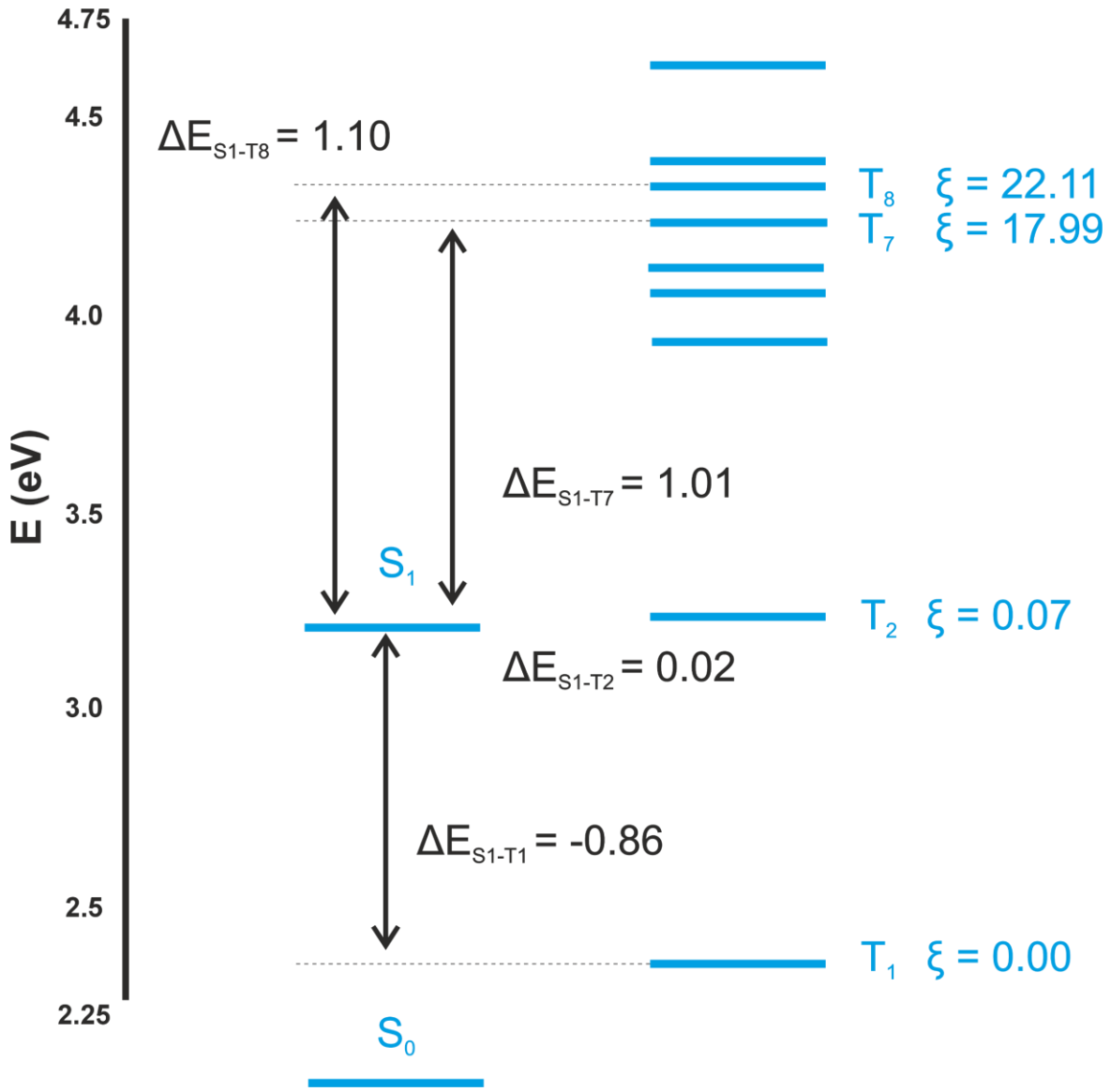
$n \rightarrow \pi^*$

T_9:

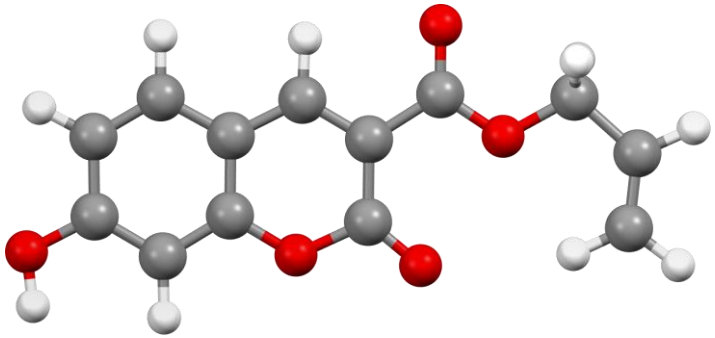


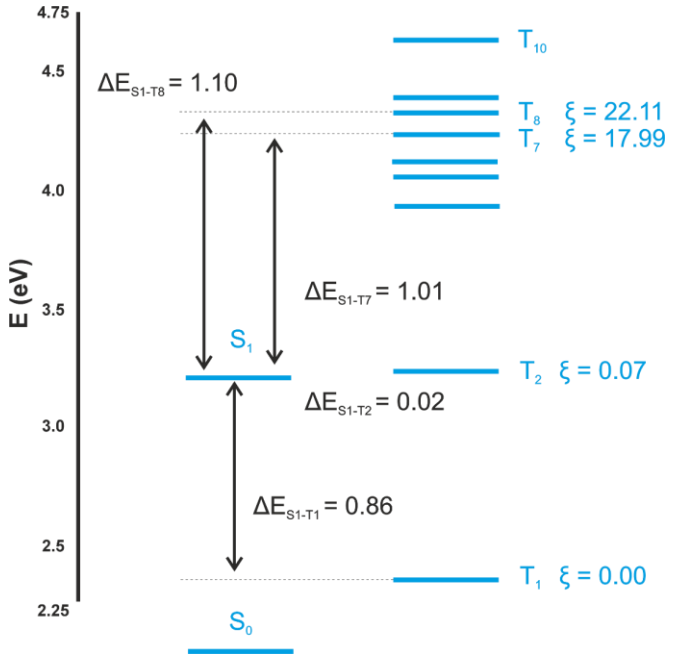
$n \rightarrow \pi^*$

ξ / cm^{-1}
ΔE / eV


4.75
4.5
4.0
3.5
3.0
2.5
2.25
E (eV)
ΔE$_{S1-T8}$ = 1.10
ΔE$_{S1-T7}$ = 1.01
ΔE$_{S1-T2}$ = 0.02
ΔE$_{S1-T1}$ = -0.86
S$_1$
S$_0$
T$_8$ ξ = 22.11
T$_7$ ξ = 17.99
T$_2$ ξ = 0.07
T$_1$ ξ = 0.00

II

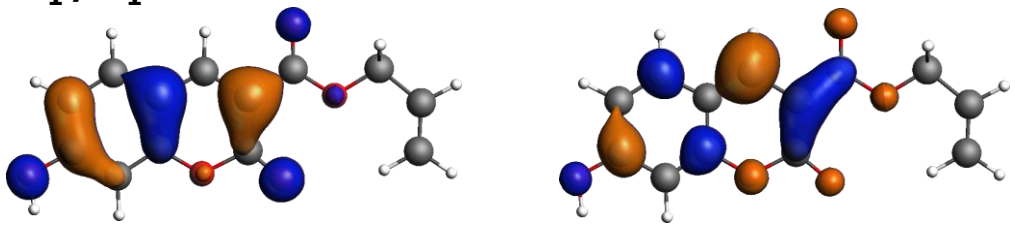




$^1(\pi, \pi^*) \rightarrow {}^3(n, \pi^*)$

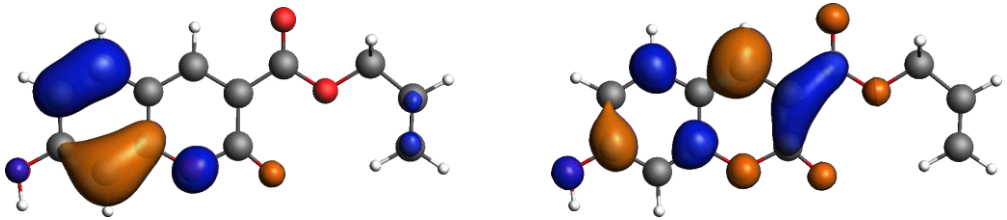
$^1(\pi, \pi^*) \rightarrow {}^3(\pi, \pi^*)$

S_1 / T_1:



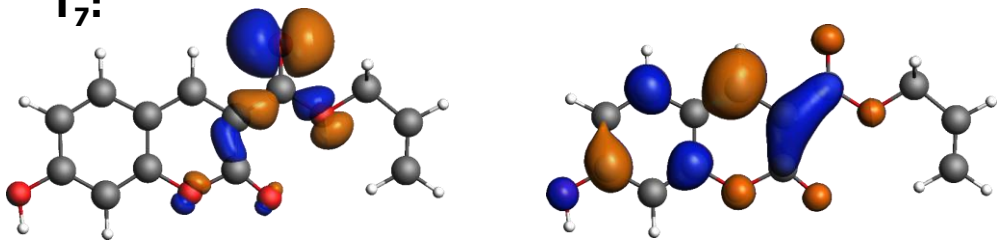
$\pi \rightarrow \pi^*$

T_2:



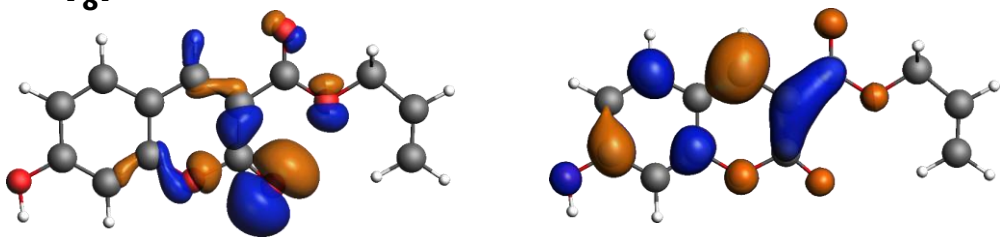
$\pi \rightarrow \pi^*$

T_7:



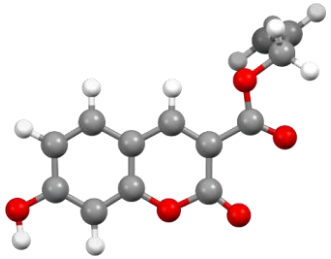
$n \rightarrow \pi^*$

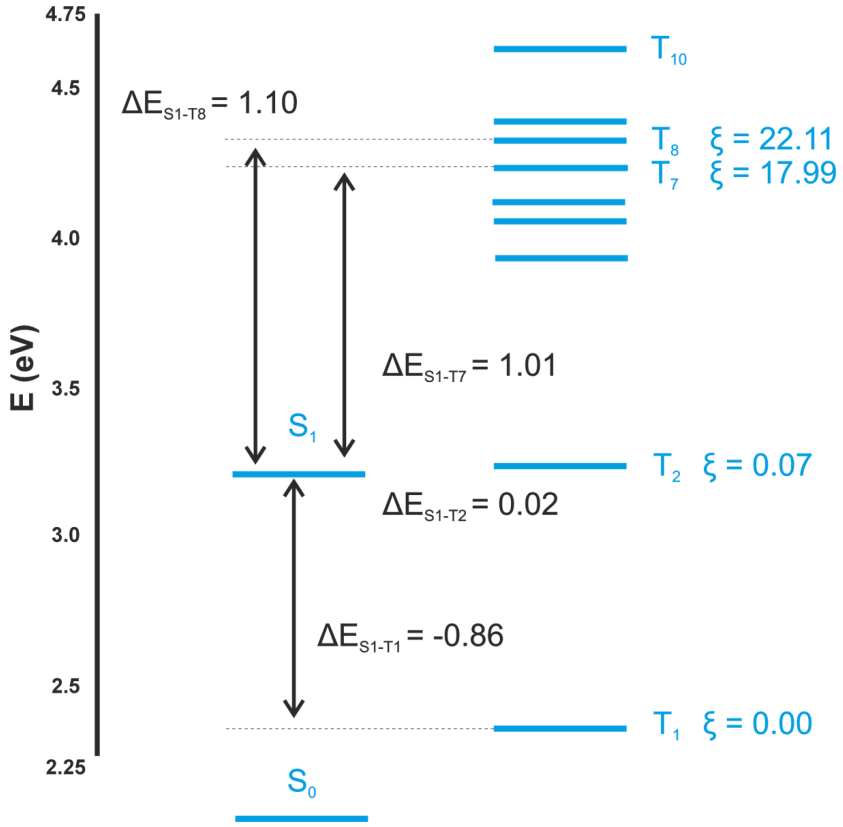
T_8:



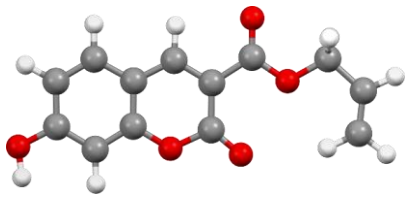
$n \rightarrow \pi^*$

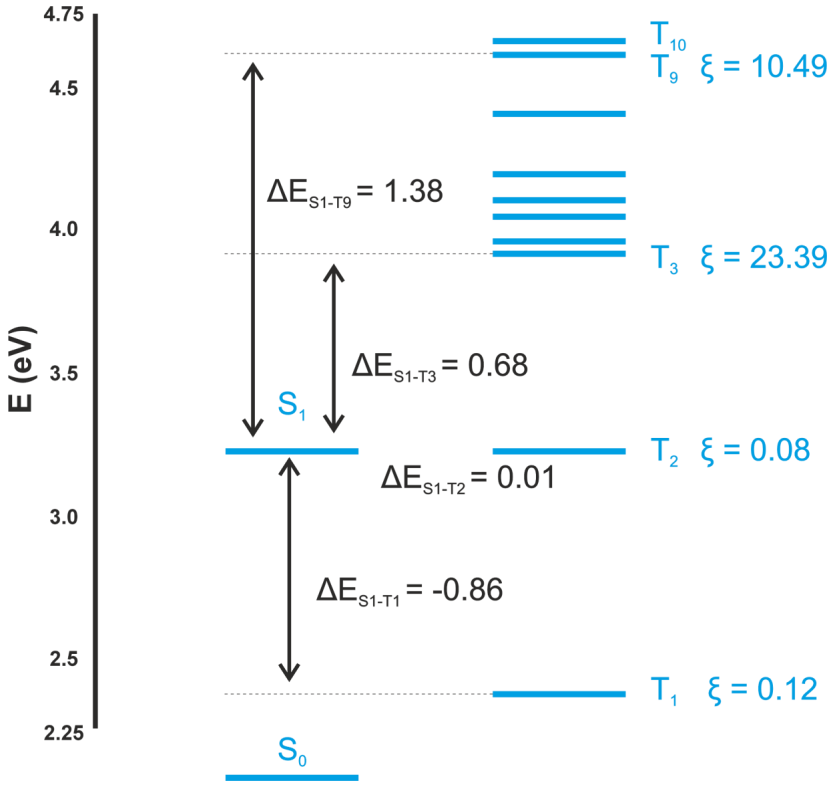
I





II





ξ / cm^{-1}
ΔE / eV

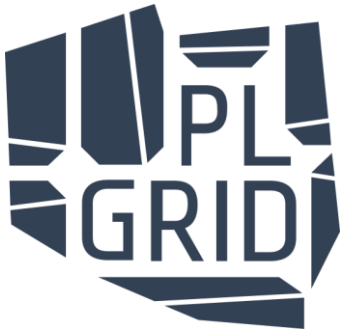
TD-DFT B3LYP//TZ2P @ B3LYP geometries

- conformational analysis of pristine molecule indicates that in solution various rotameric structures with similar populations may co-exist

- fluorescence emission energies computed for different conformers change rather negligibly with changes in ester substituent arrangement and seem to correspond well to higher-energy signal in the experimental fluorescence spectrum:
  - TD-DFT tends to overestimate it
  - CCSD provides quantitative agreement with the measured value
  - in each case $S_1 \rightarrow S_0$ corresponds to ππ* transition within the coumarin ring

- DF effect cannot be explained based on co-existence of various rotameric structures → further research: aggregation, explicit solvent effects

- obtained SOC values indicate strong impact of the position of the carbonyl group in esther relative to the coumarin ring on ISC efficiency and thus occurence of RTP → further research: CCSD validation, phoshporescence emission studies



We gratefully acknowledge Polish high-performance computing infrastructure PLGrid (HPC Center: ACK Cyfronet AGH) for providing computer facilities and support within computational grant no. PLG/2024/017662.

Finding best interaction for systems

Program: ORCA
Method: DOCKER (energy driven algorithm)

S_0 optimization

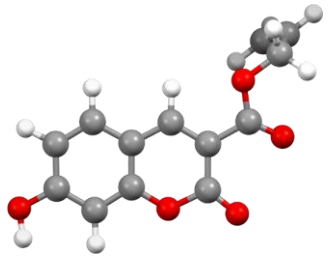
Program: Gaussian 16
Method: DFT
Functional: B3LYP + D3BJ
Basis set: 6-311++G(d,p)
Environment: PCM (methanol, ε = 32.6)

S_1 optimization

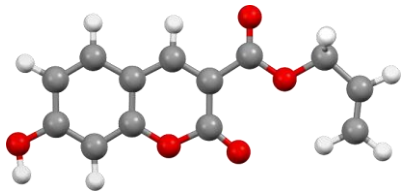
Program: Gaussian 16/ORCA
Method: (TD)-DFT
Functional: B3LYP (+ D3BJ), ωB97X-D
Basis set: 6-311++G(d,p)
Environment: PCM (methanol, ε = 32.6)

DFT B3LYP + D3BJ//6-311++G(d,p)

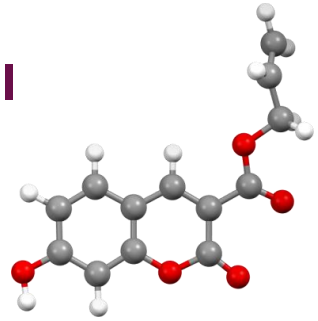
I



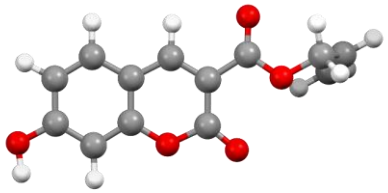
II



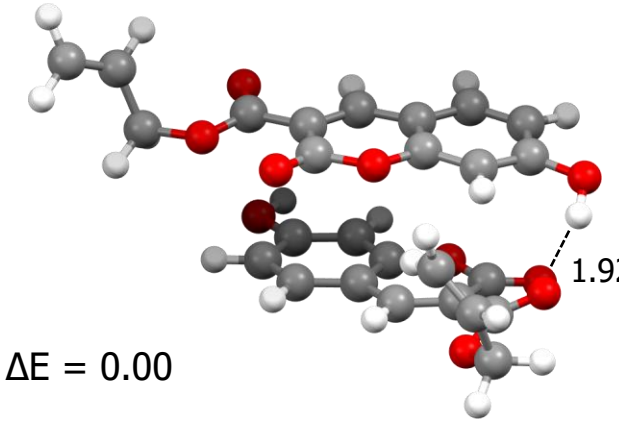
III



V

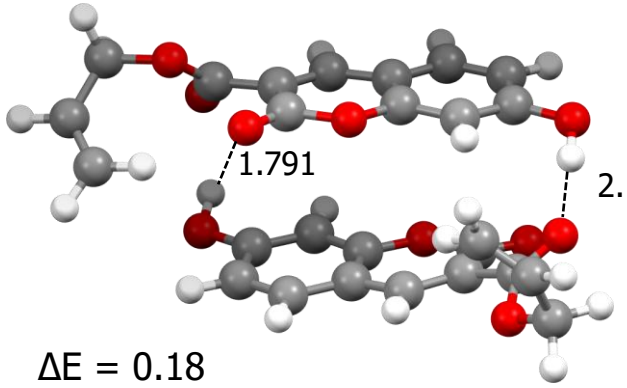


I + III



ΔE = 0.00

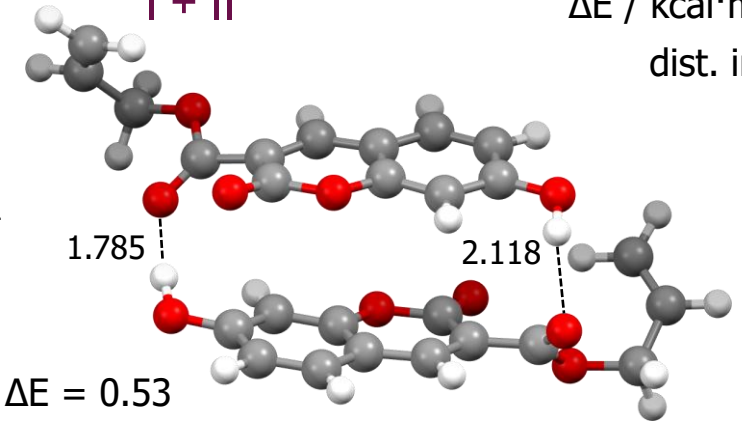
I + IV



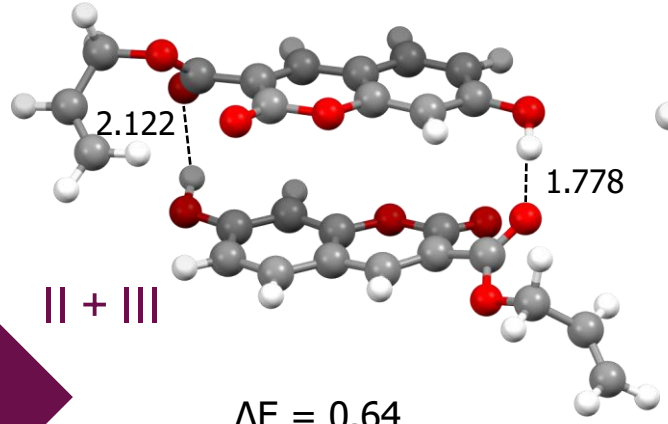
ΔE = 0.18

I + II

ΔE / kcal·mol^{-1}
dist. in Å

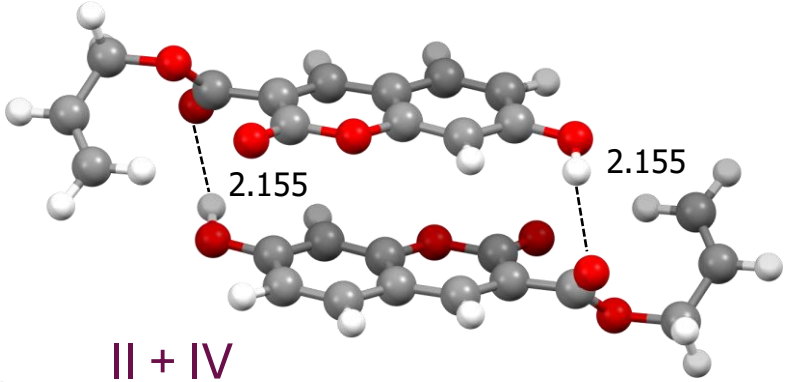


ΔE = 0.53



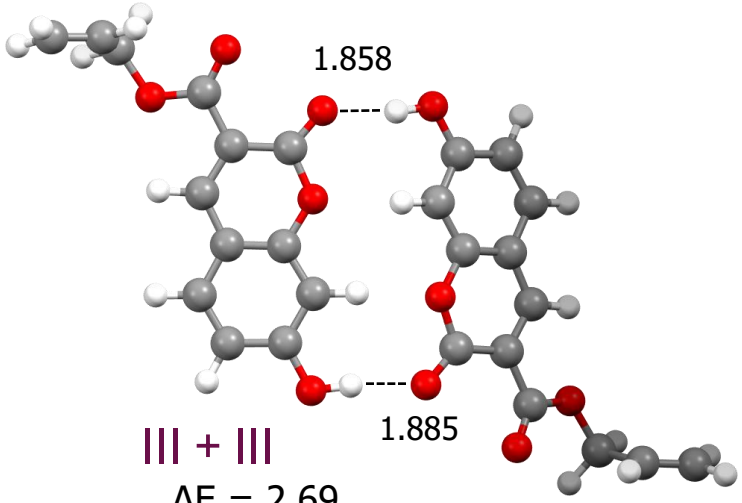
II + III

ΔE = 0.64



II + IV

ΔE = 2.46



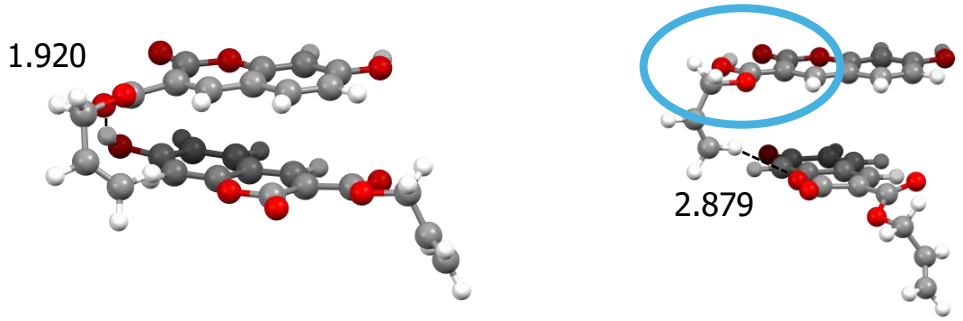
III + III

ΔE = 2.69

S0 **S1**

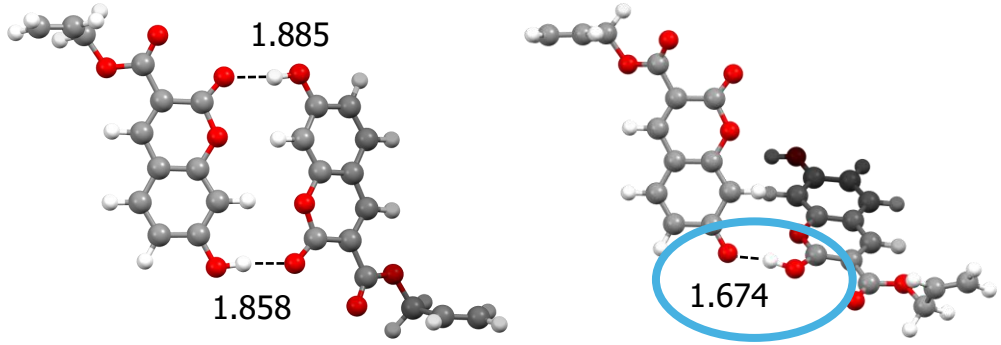
B3LYP **B3LYP**

I



ΔE = 0.00

VI



ΔE = 4.08

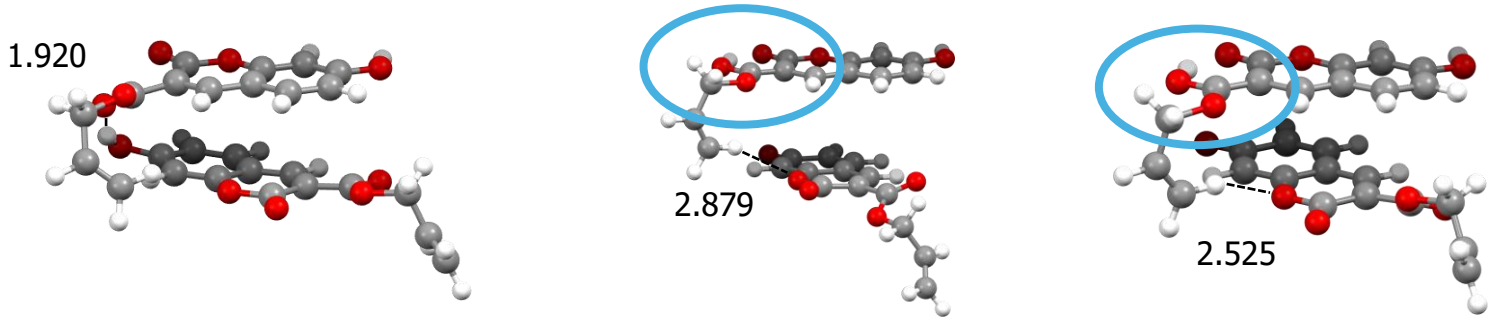
ΔE / kcal·mol^{-1}

dist. in Å, λ in nm

S0 **S1**

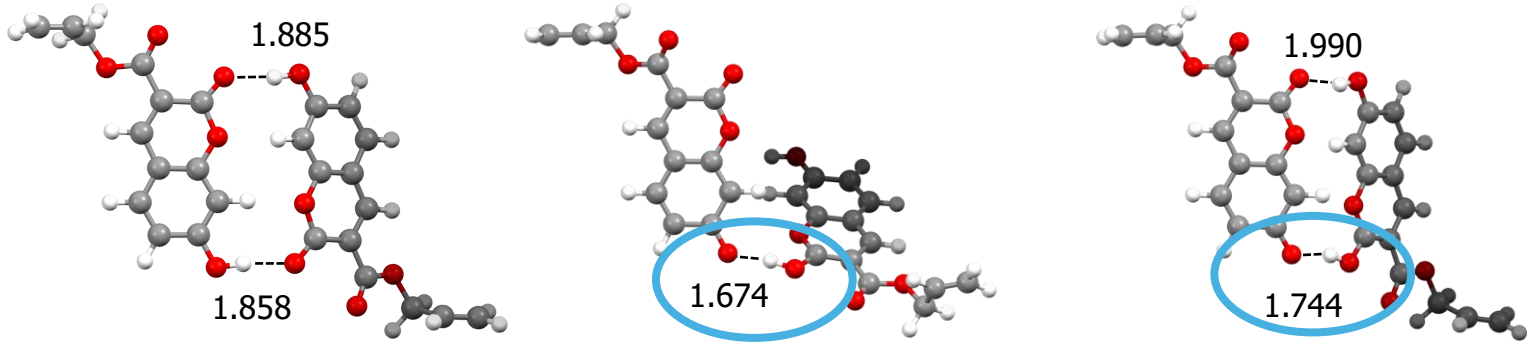
B3LYP **B3LYP** **B3LYP + D3BJ**

I



ΔE = 0.00 ΔE = 0.00

VI



ΔE = 4.08 ΔE = 13.25

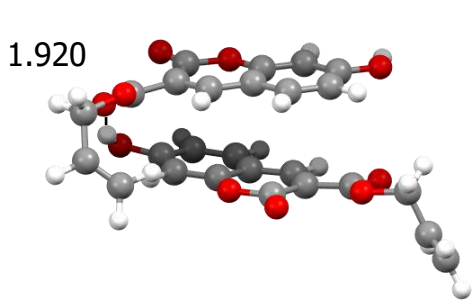
ΔE / kcal·mol^{-1}

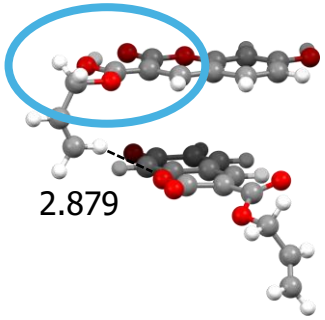
dist. in Å, λ in nm

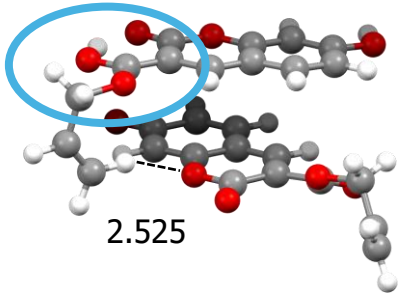
S0 **S1**

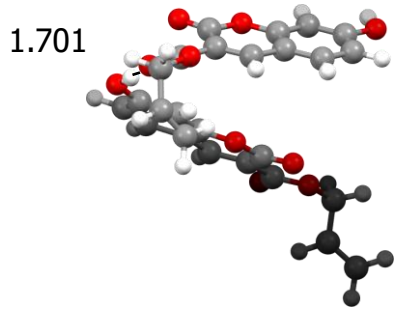
B3LYP **B3LYP** **B3LYP + D3BJ** **ωB97X-D**

I



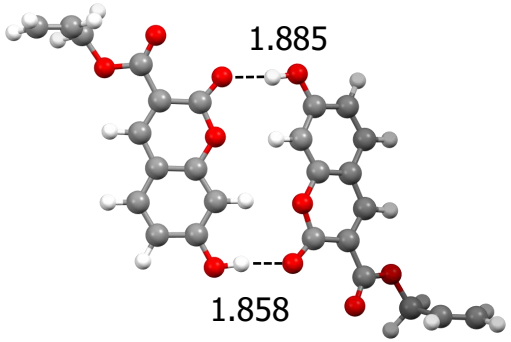


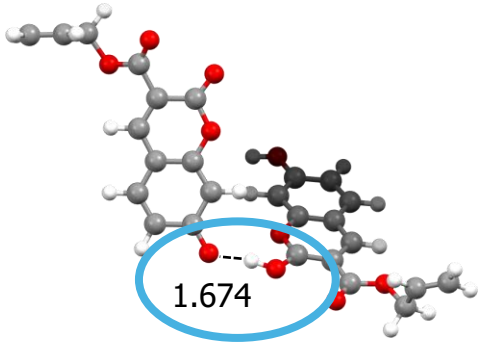


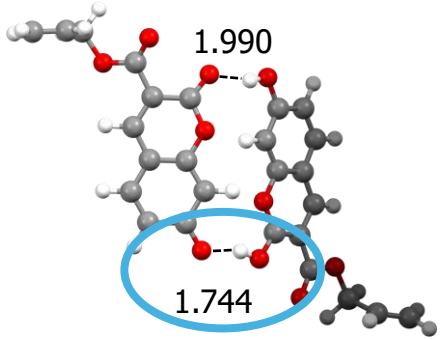


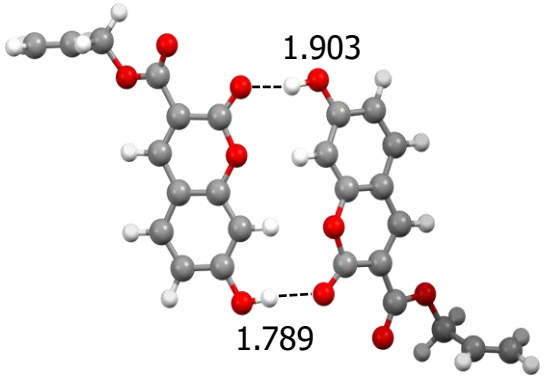
ΔE = 0.00 ΔE = 0.00 ΔE = 0.51

VI









ΔE = 4.08 ΔE = 13.25 ΔE = 0.00

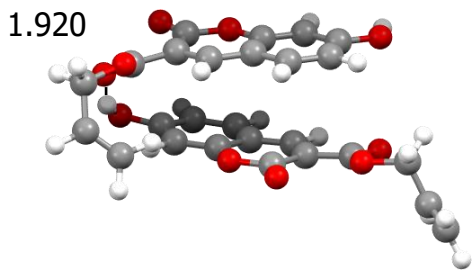
ΔE / kcal·mol^{-1}

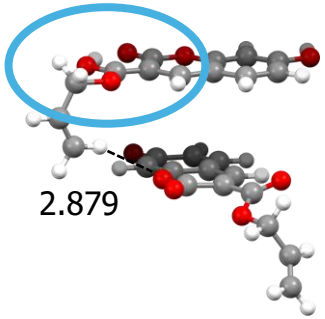
dist. in Å, λ in nm

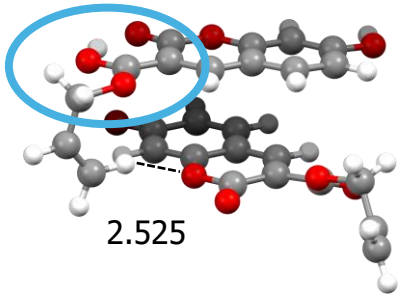
S0 **S1**

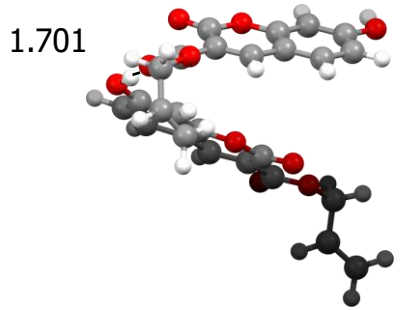
B3LYP **B3LYP** **B3LYP + D3BJ** **ωB97X-D**

I







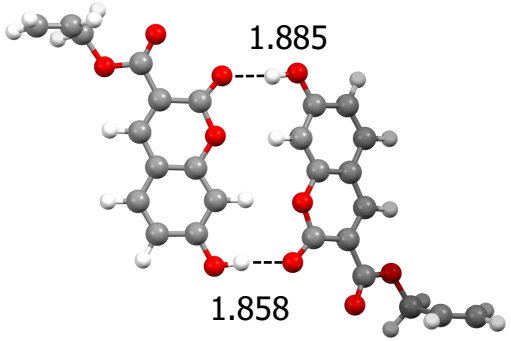


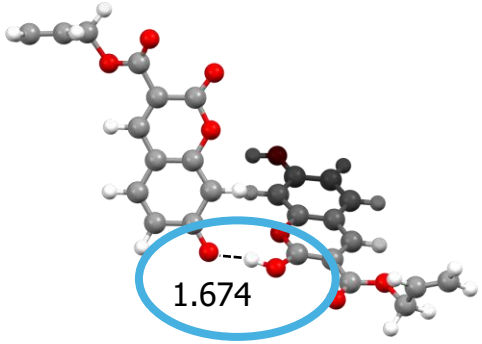
ΔE = 0.00 λ = 1830

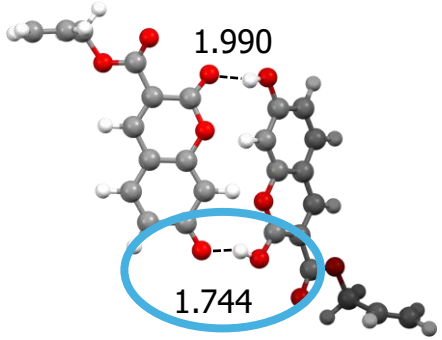
ΔE = 0.00 λ = 1723

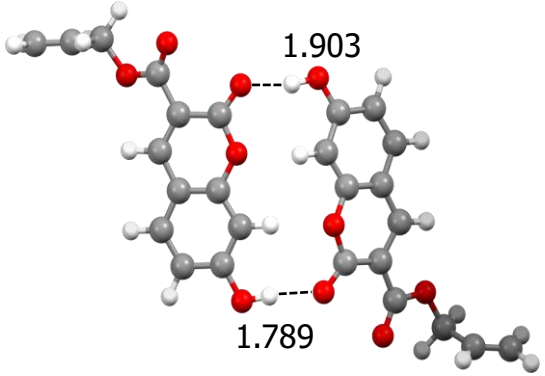
ΔE = 0.51 λ = 369

VI









ΔE = 4.08 λ = 978

ΔE = 13.25 λ = 909

ΔE = 0.00 λ = 375

ΔE / kcal·mol^{-1}

dist. in Å, λ in nm