Group seminar 25, 10, 2019

Effects of Polarity and Polarizability of Solvent on 9,9’-Bifluorenylidene Molecular Balance

Yu Ozawa

Hokkaido University

- located in Sapporo
- 18600 students
- 680 professors
- one Nobel prize

Prof.
Akira Suzuki
(2010)

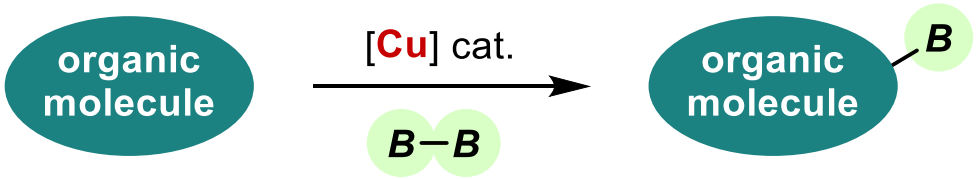
Sapporo

Japan

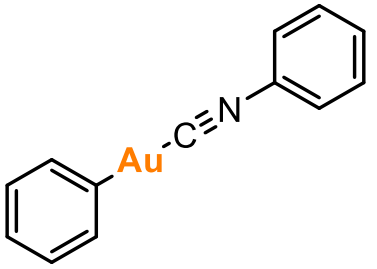
Ito Group

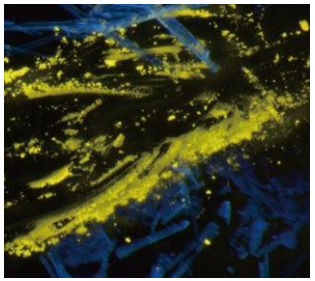
Prof. Hajime Ito

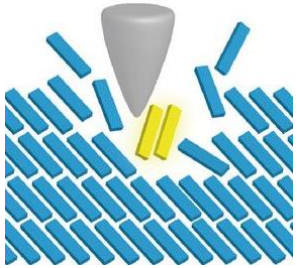
1. Copper(I)-catalyzed borylation reaction



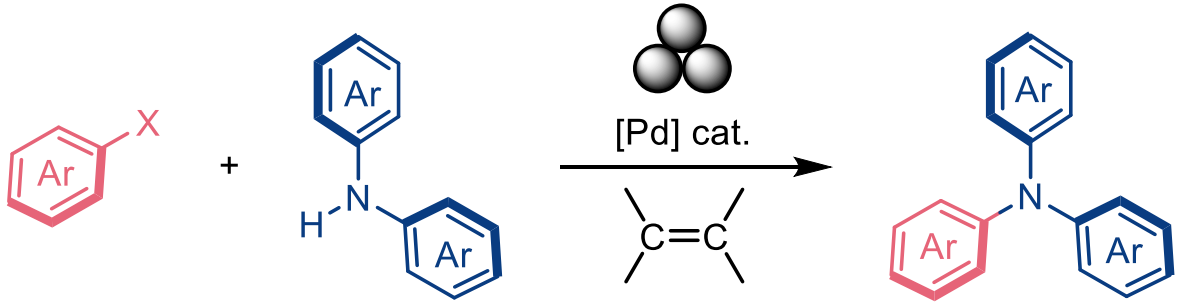
2. Mechano-responsive phosphorescent gold(I) complex



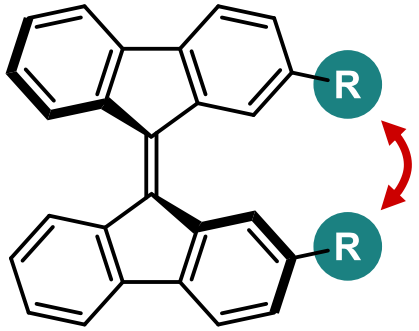




3. Synthetic mechanochemistry



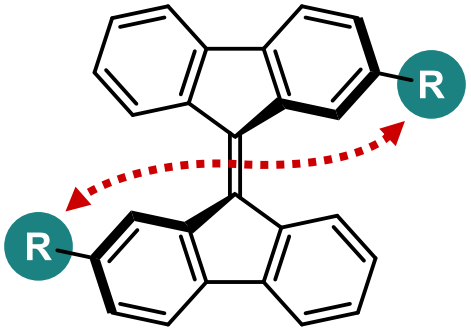
Molecular Balance based on 9,9’-Bifluorenylidene



(*Z*)-**1**

Intramolecular interaction

hv or Δ

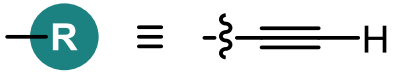


(*E*)-**1**

No interaction

- steric repulsion
- dispersion interaction
- dipole moment
- hydrogen bonding
- C−H/π interaction
- entropy effect

This work

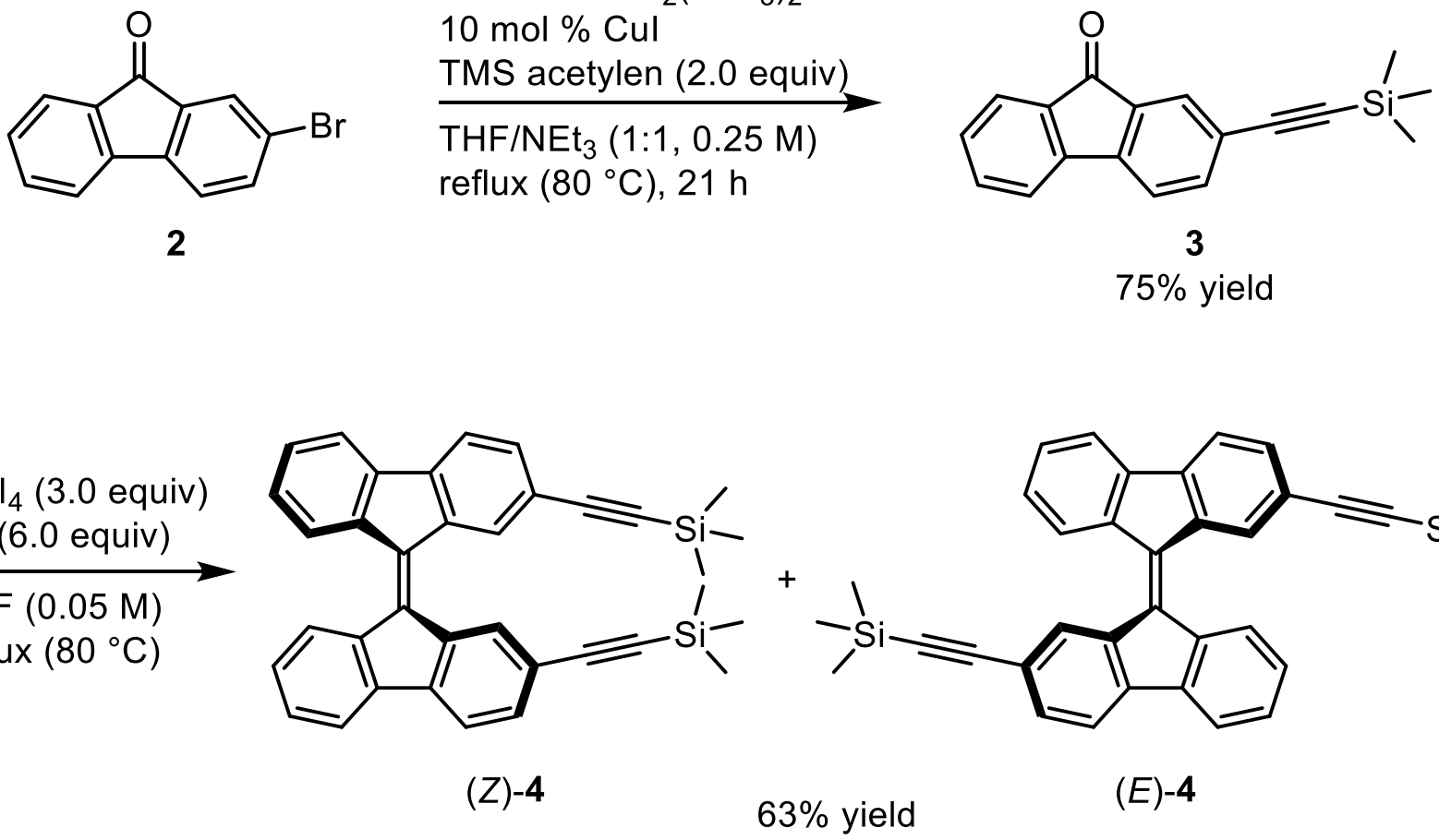


terminal alkyne

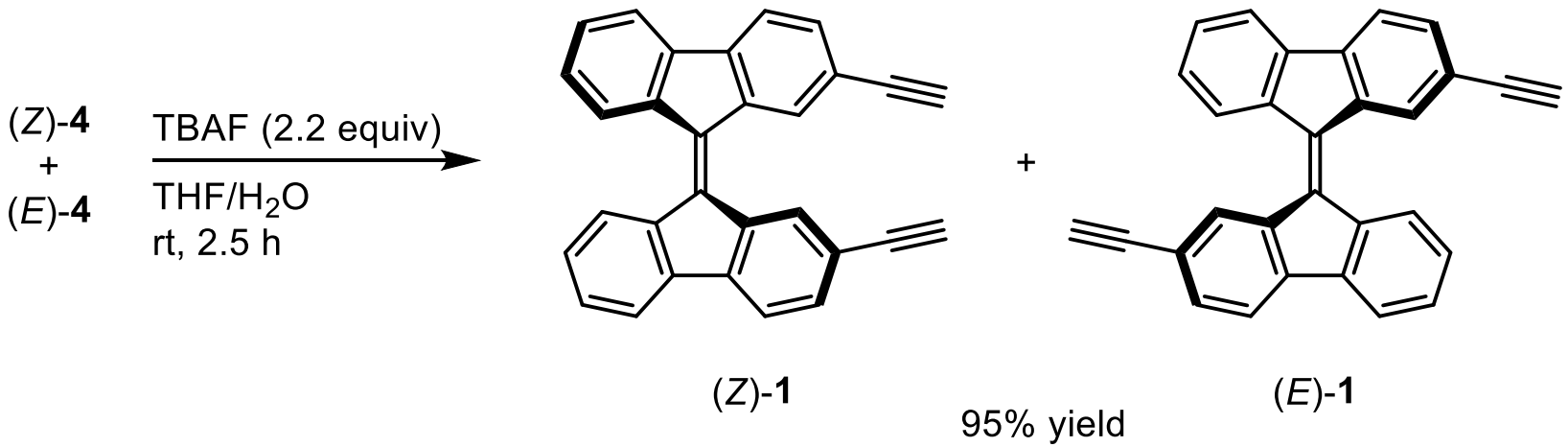
- smallest functional group in hydrocarbon
- rigid functional group
- stand-out dipole moment effect (hypothesis)

Minabe, M.; Oba, T.; Tanaka, M.; Kanno, K.; Tsubota, M. *Chem. Lett.* **2000**, *1*, 498.
Minabe, M.; Yamazaki, A.; Imai, T.; Takanezawa, T.; Karikomi, M. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1758.

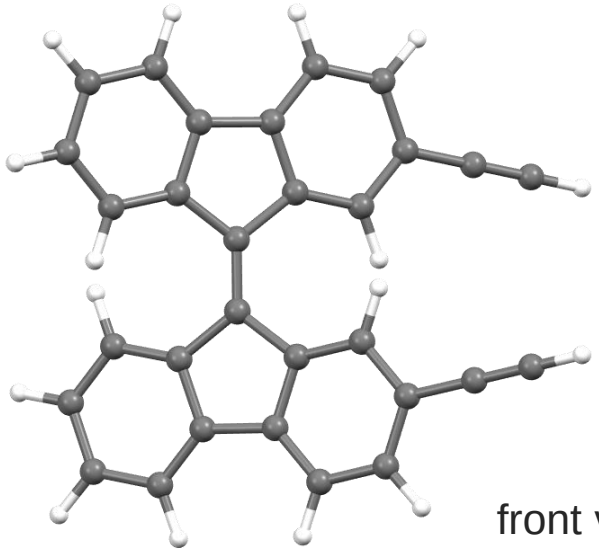
Synthesis of (*Z*)- and (*E*)-1



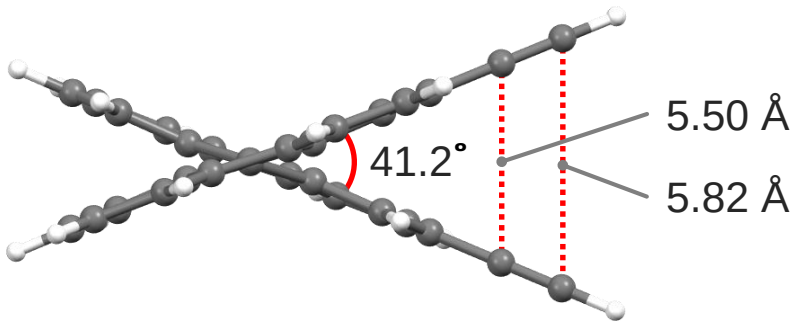
Synthesis of (*Z*)- and (*E*)-1



Calculated structure of (*Z*)-1



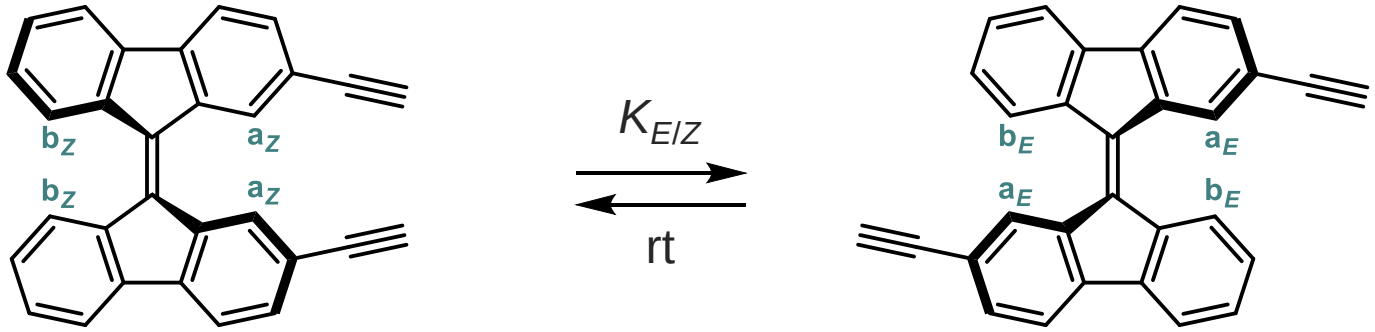
front view



side view

DFT method: B3LYP-D3(BJ)/cc-pVDZ/gas phase.

Thermo-isomerization of (*Z*)- and (*E*)-1



(*Z*)-**1** (*E*)-**1**

Definitions

$$K_{E/Z} = \frac{[(E)\text{-}\mathbf{1}]}{[(Z)\text{-}\mathbf{1}]}$$

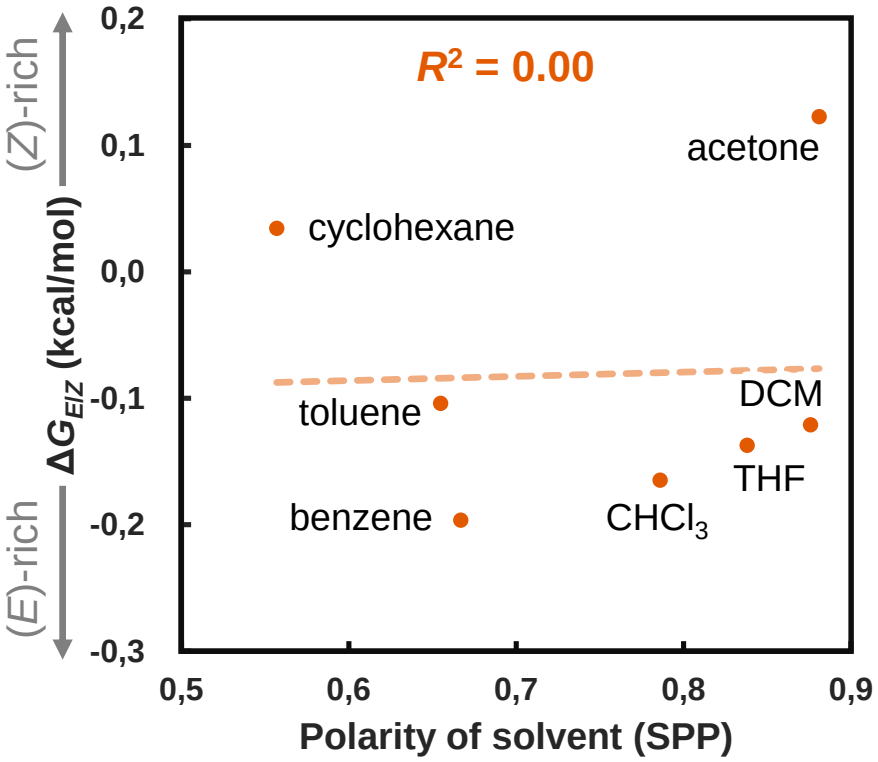
$$\Delta G_{E/Z} = G_E - G_Z$$
$$= -RT \ln(K_{E/Z})$$

Procedure of NMR study

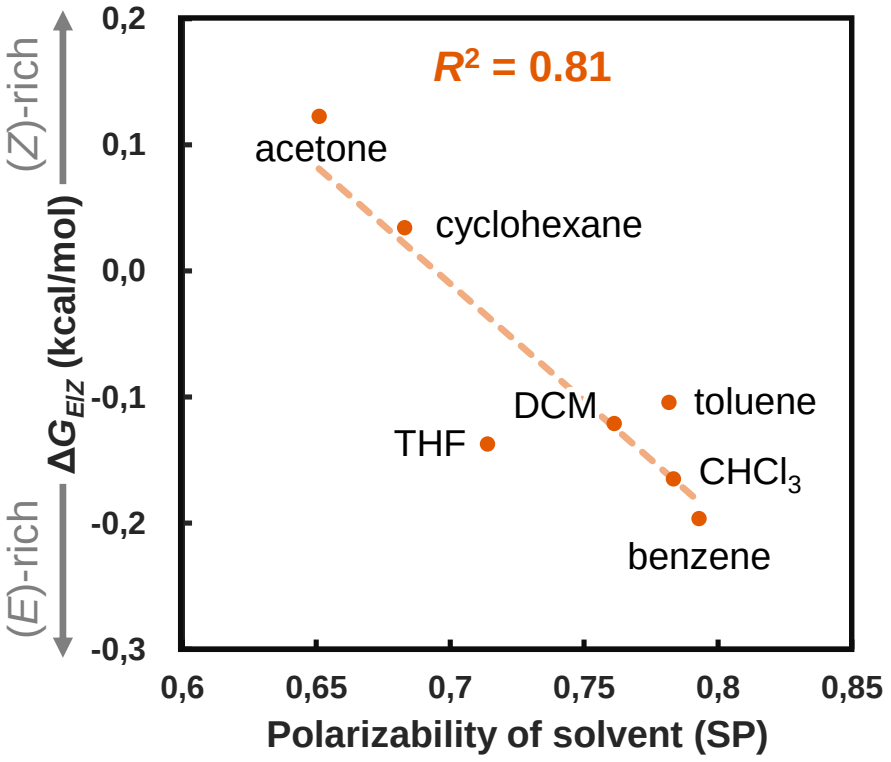
1. prepare the almost saturated NMR samples.
2. keep the sample dark at r.t. for 24−72 h.
3. take ^{1}H NMR five times.
4. calculate $K_{E/Z}$ according to the following eq.

$$K_{E/Z} = \frac{\text{Sum of area of } \mathbf{a_E} \text{ and } \mathbf{b_E}}{\text{Sum of area of } \mathbf{a_Z} \text{ and } \mathbf{b_Z}}$$

Results



No correlation

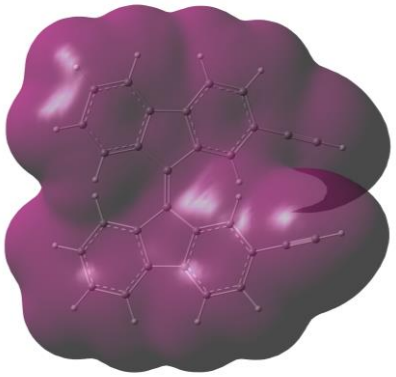


Medium negative correlation

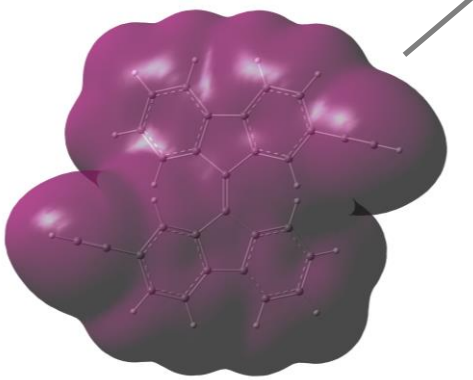
Catalán, J.; Hopf, H. *Eur. J. Org. Chem.* **2004**, *2004*, 4694.

Insight into Effect of Polarizability of Solvent

1. Difference of solvent contacting surface (Δ*S*)



(*Z*)-**1**
Δ*S* = 0.00 Å^2

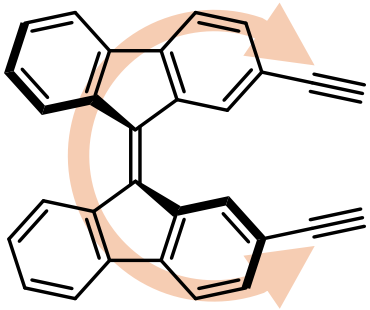


isosurface of electron density at 0.0001

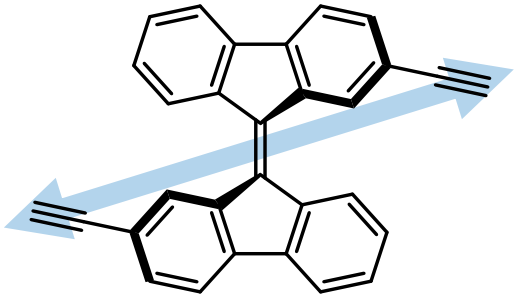
(*E*)-**1**
Δ*S* = 2.55 Å^2

DFT method: B3LYP-D3(BJ)/Def2-TZVPP/gas phase//B3LYP-D3(BJ)/cc-pVDZ/gas phase.

2. Difference of length of π-system



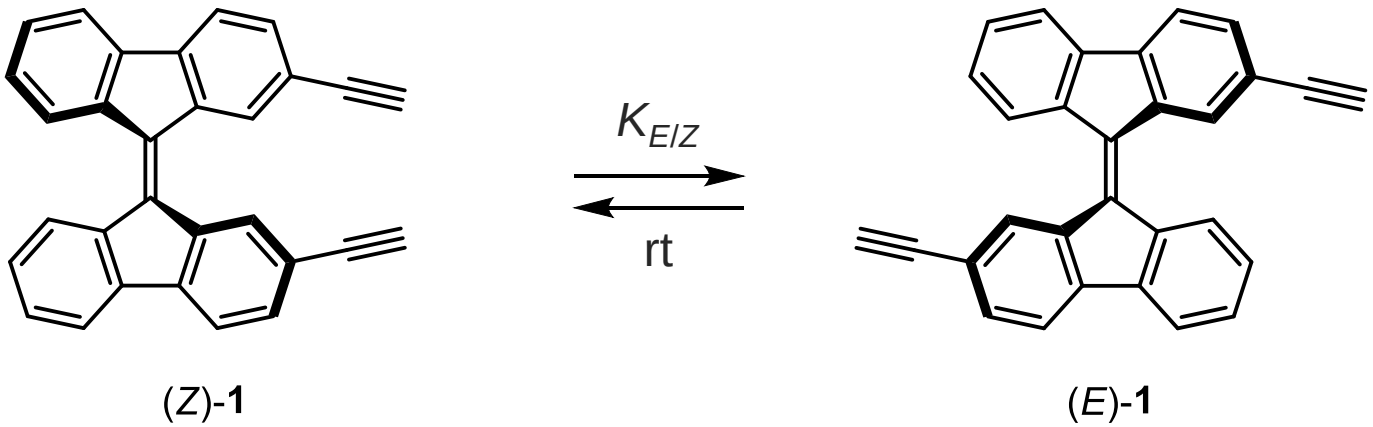
(*Z*)-**1**



(*E*)-**1**

larger solvent contacting surface
wider π-system
are stabilized in polarizable solvent

Summary



non-polarizable solvent *polarizable solvent*

- polarizability of solvents affects the equilibrium constant $K_{E/Z}$
- dipole moment of the molecule is not important contrary to expectation
- dispersion interaction between the molecule and solvents is important

Acknowledgement

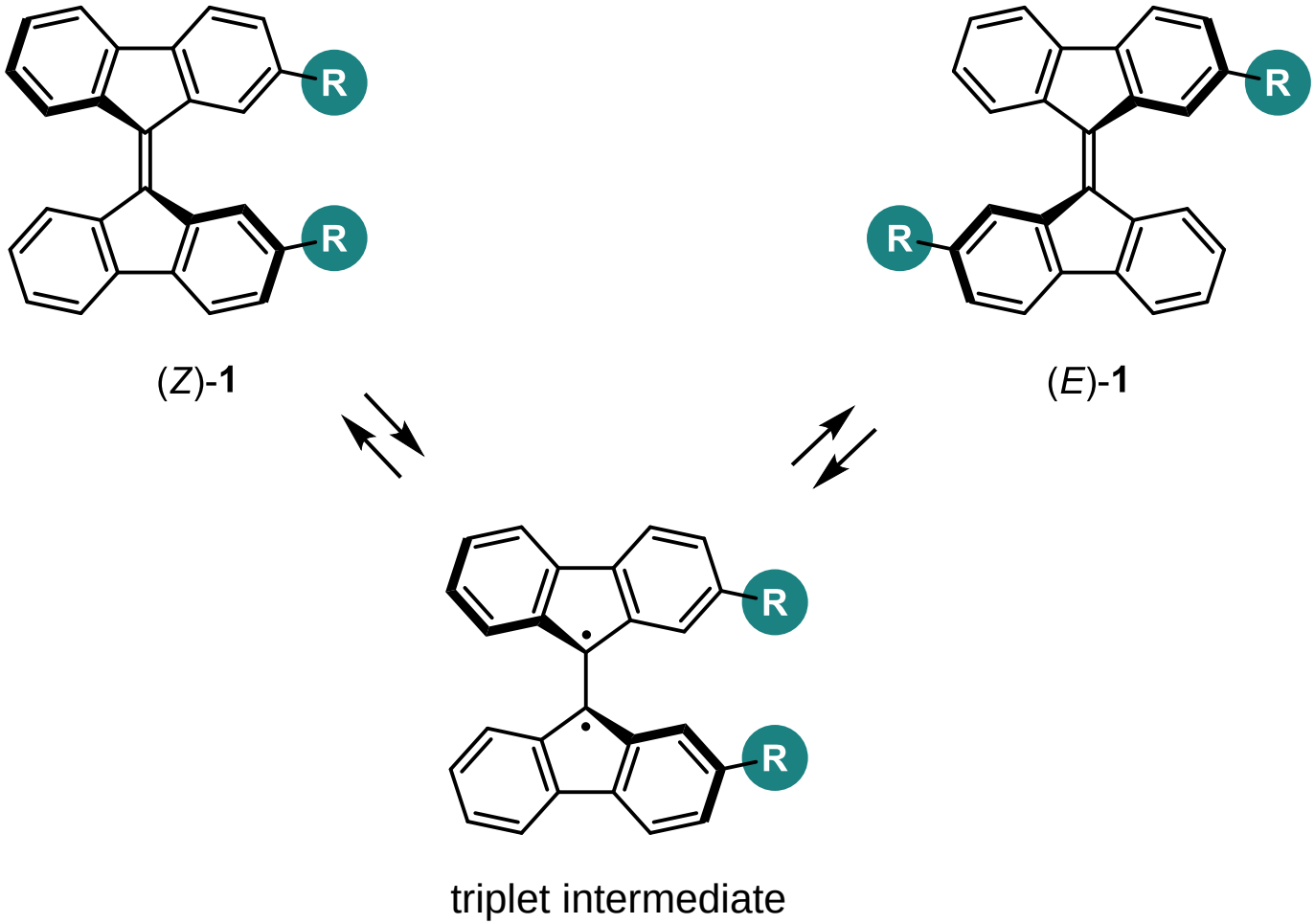
Prof. Peter R. Schreiner

Mr. Finn M. Wilming

All members in PRS group

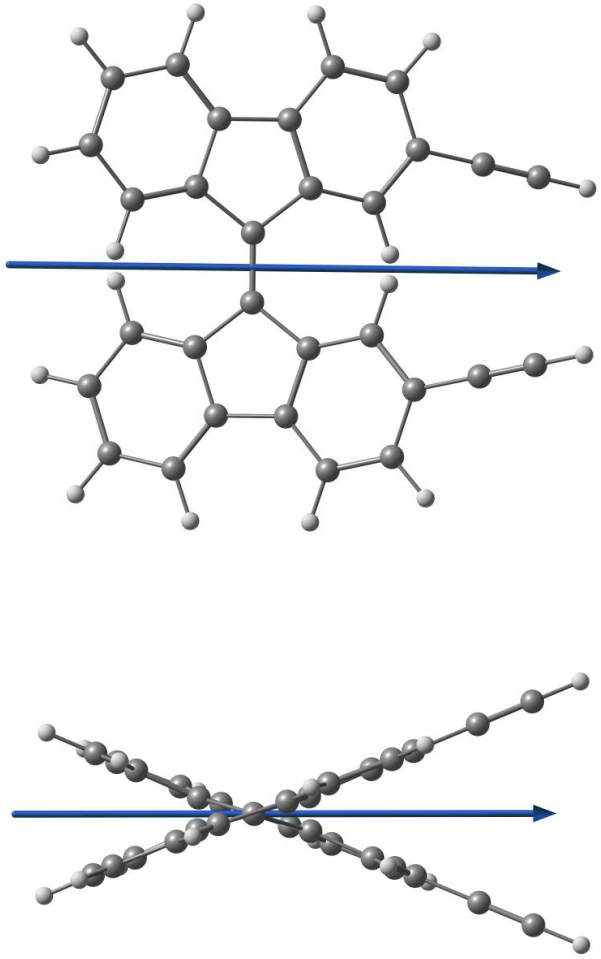
Analytics team in Justus Liebig University

Isomerization Pathway

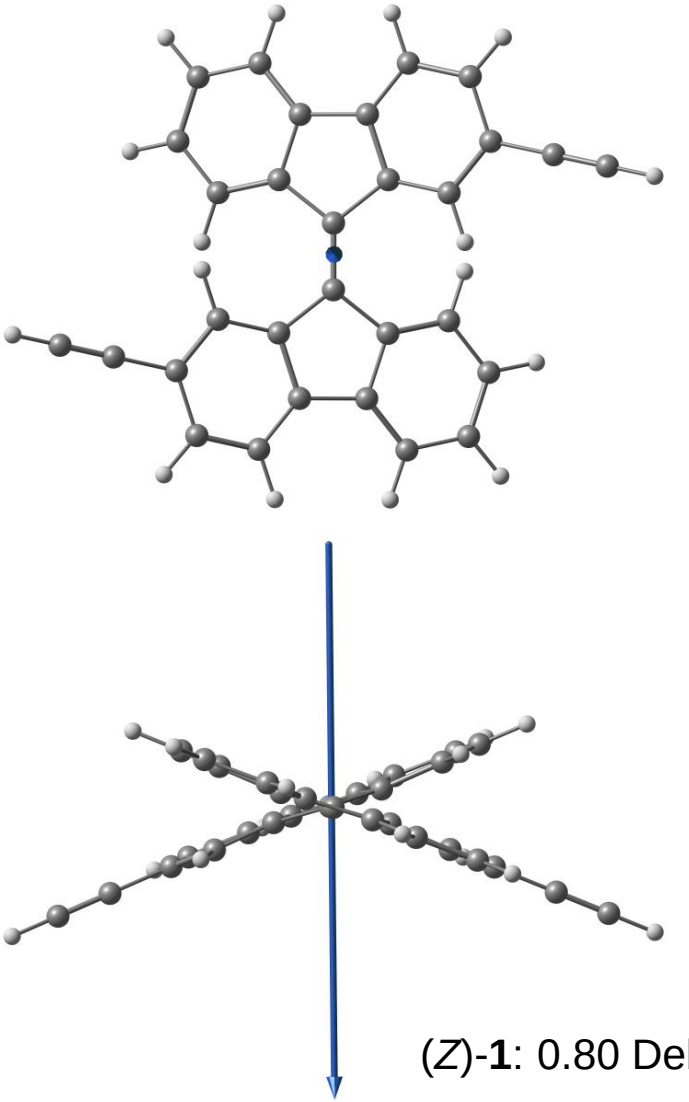


Gault, I. R.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. D* **1970**, 269.
Minabe, M.; Yamazaki, A.; Imai, T.; Takanezawa, T.; Karikomi, M. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1758.

Dipole Moments of (*E*)- and (*Z*)-1



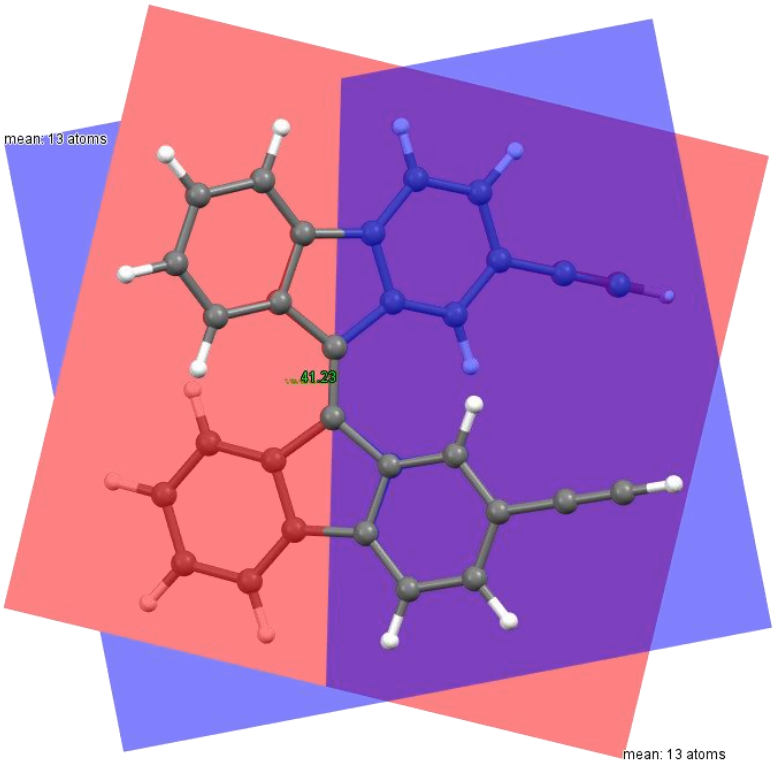
(*E*)-**1**: 1.72 Debye

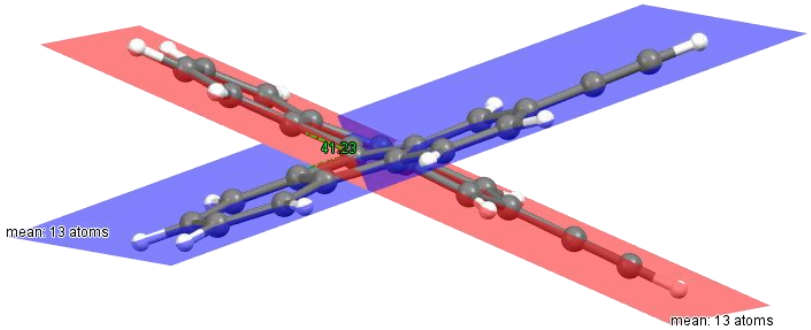


(*Z*)-**1**: 0.80 Debye

DFT method: B3LYP-D3(BJ)/Def2-TZVPP/gas phase//B3LYP-D3(BJ)/cc-pVDZ/gas phase.

Angle between Two Fluorene Planes in (*Z*)-1

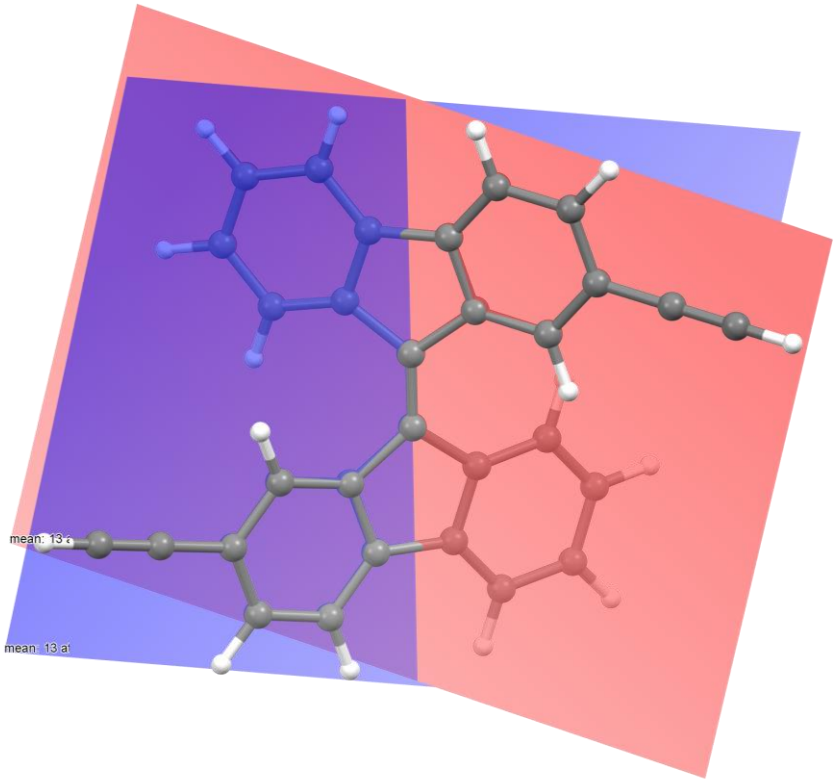


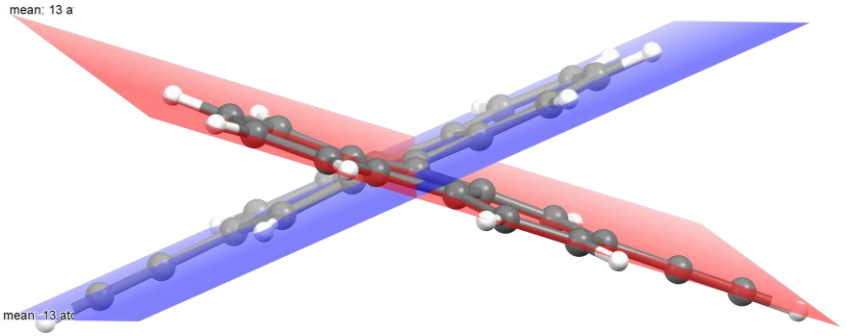


41.2˚

DFT method: B3LYP-D3(BJ)/cc-pVDZ/gas phase.

Angle between Two Fluorene Planes in (*E*)-1

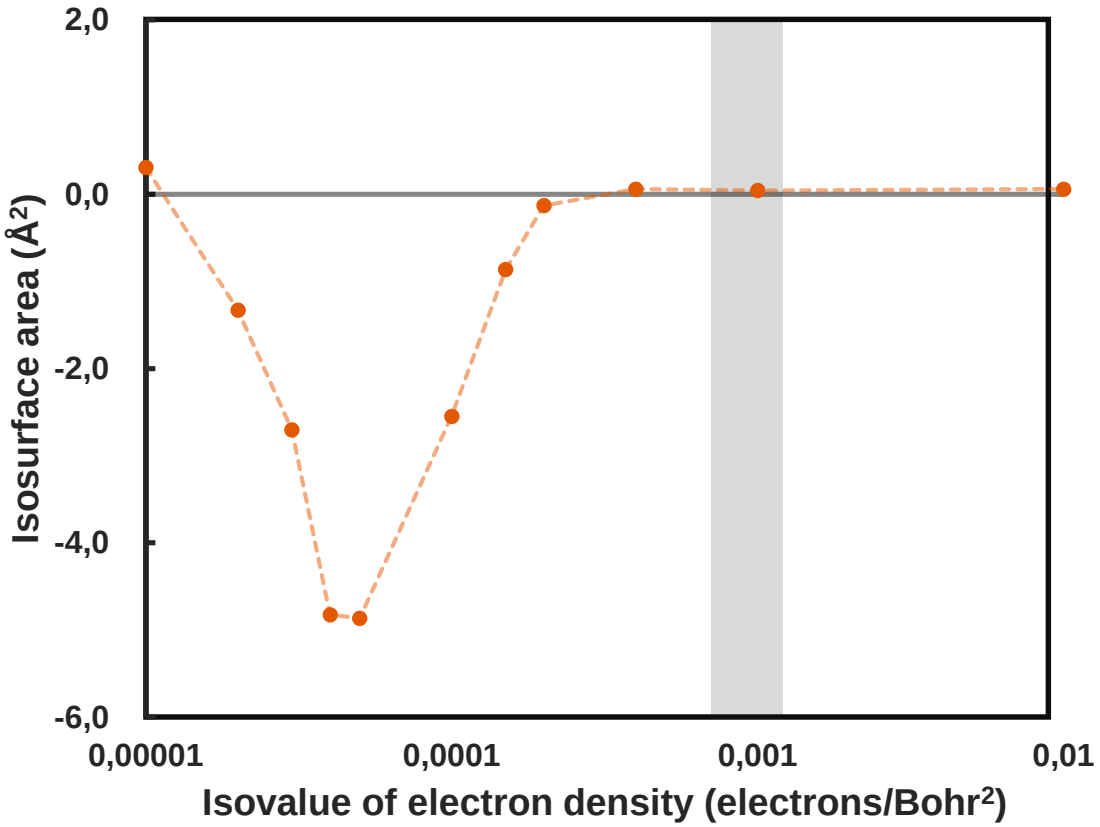




41.1˚

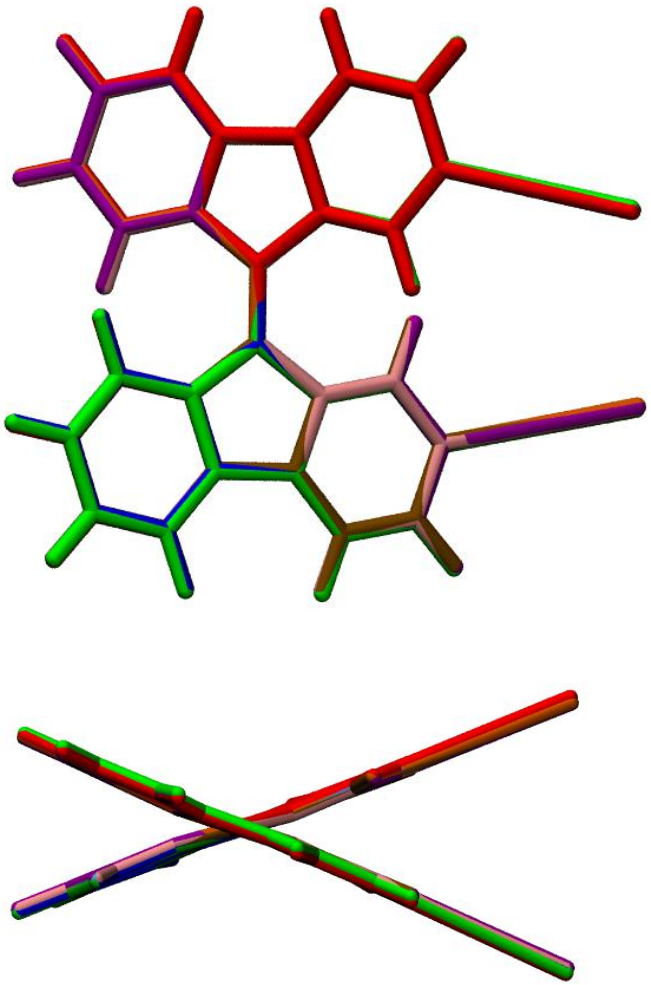
DFT method: B3LYP-D3(BJ)/cc-pVDZ/gas phase.

Isosurface of Electron Density



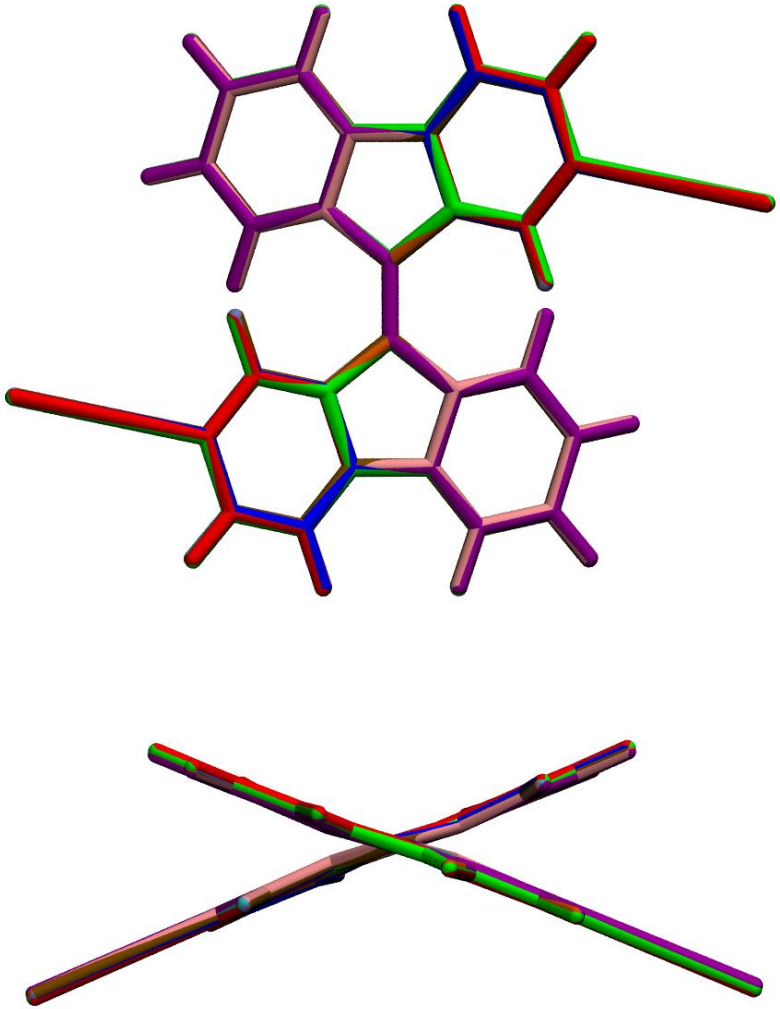
DFT method: B3LYP-D3(BJ)/Def2-TZVPP/gas phase//B3LYP-D3(BJ)/cc-pVDZ/gas phase.

Screening of DFT Method for (*Z*)-isomer



- B3LYP/6-31G(d)
- B3LYP/cc-pVDZ
- B3LYP/Def2-SVP
- B3LYP-D3(BJ)/6-31G(d)
- B3LYP-D3(BJ)/cc-pVDZ
- B3LYP-D3(BJ)/Def2-SVP
- ωB97XD/6-31G(d)
- ωB97XD/cc-pVDZ
- ωB97XD/Def2-SVP
- M06-2X/6-31G(d)
- M06-2X/cc-pVDZ
- M06-2X/Def2-SVP

Screening of DFT Method for (*E*)-isomer



- B3LYP/6-31G(d)
- B3LYP/cc-pVDZ
- B3LYP/Def2-SVP
- B3LYP-D3(BJ)/6-31G(d)
- B3LYP-D3(BJ)/cc-pVDZ
- B3LYP-D3(BJ)/Def2-SVP
- ωB97XD/6-31G(d)
- ωB97XD/cc-pVDZ
- ωB97XD/Def2-SVP
- M06-2X/6-31G(d)
- M06-2X/cc-pVDZ
- M06-2X/Def2-SVP