Role of Symmetry in Environment-Sensing Mechanism of BODIPY-Based Molecular Dyes

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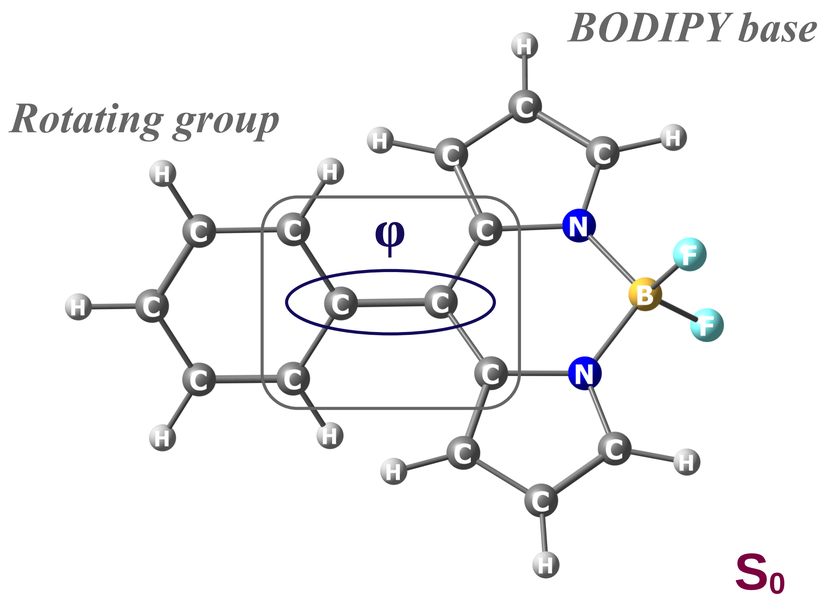
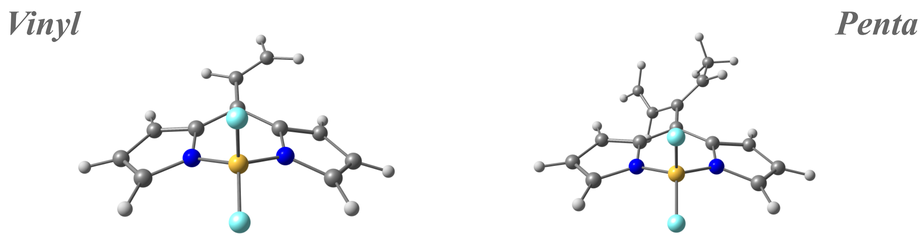
Looks good?

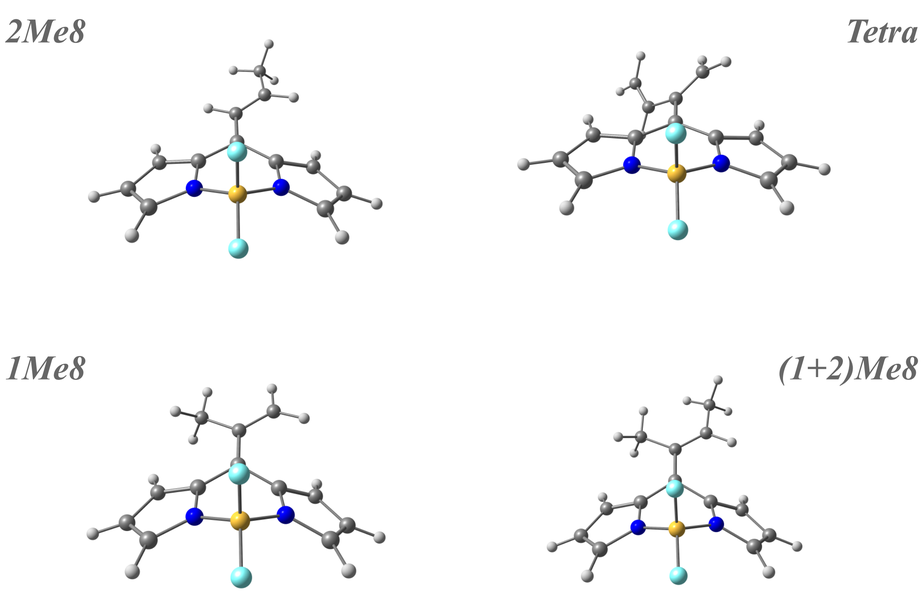


Computations

- Resources of Vilnius University OAC "**VU HPC** | **Saulėtekis**"
- Computations performed by *Gaussian16* program package
- Ground-state and time-dependent density functional theory
- **M06-2X** correlation-exchange functional, **cc-pVDZ** atomic basis set
- Solvent field effects included using **C-PCM** (toluene)

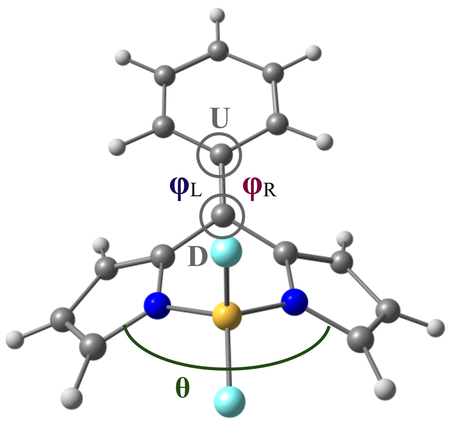
What about non-symmetric rotation groups?



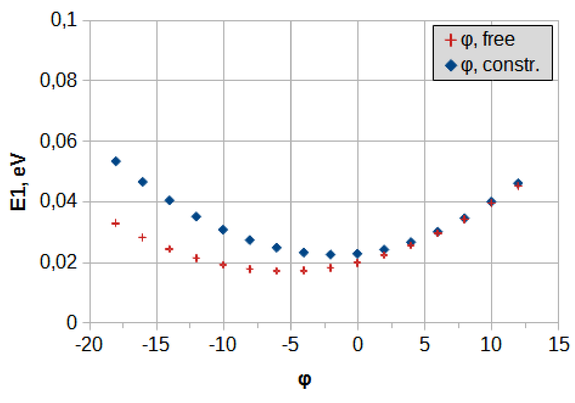


Well…

(near) **S_{1r}**



$\varphi_L = +5{,}5\ °$
$\varphi_R = -6{,}0\ °$
$o.o.p._U = 2{,}8\ °$
$o.o.p._D = 7{,}7\ °$
$\theta \approx 135\ °$



Modeling reaction coordinate

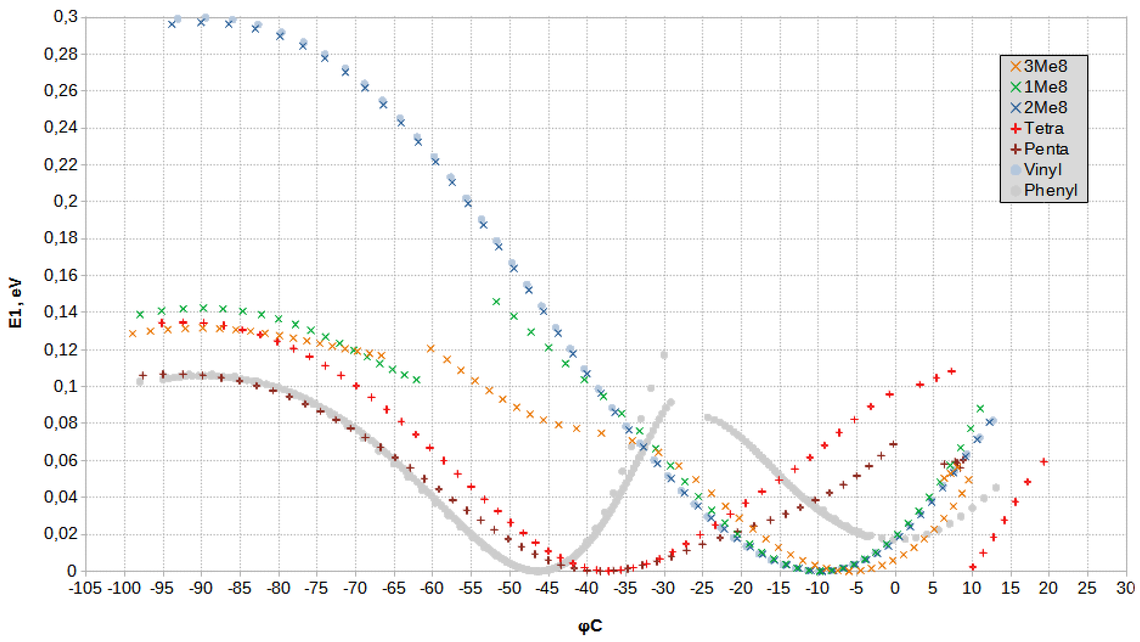
Single rotation angle approximations:
- **Free** (unconstrained) scanning at fixed φ_R values
- **Constrained** scanning (keeping U and D out-of-plane angles constant)

Neither of the above results in a minimum at 0-degree angle!

- **Reasoning:** optimization space does not preserve base or rotating planes – at least not as defined by dihedral angles φ_R, φ_L

- **Correction:**

$$\varphi_C = \tfrac{1}{2}\,(\varphi_R + \varphi_L)$$



- **Validation** (BODIPY-phenyl and derivatives)

1. Toliautas *et al.*, *ChemEurJ* **25**, 10342 (2019)
2. Polita et al., *PCCP* **22**, 8296 (2020)
3. Maleckaitė *et al.*, *ChemEurJ* **27**, 16768 (2021)
4. Maleckaitė *et al.*, *Molecules* **27**, 23 (2022)

Free vs. constrained scan

Constrained: some definition of rotation area
Constrained: wrong energy values (not a full optimization)

Free: "correct" optimization
Free: some regions are difficult to sample (see e. g. phenyl barrier)

(some) Findings

1. Second vinyl group forms the rotor structure needed to shift S_1 energy minimum towards –45 ° angle values
2. Mirror symmetry of the phenyl group causes the S_1 barrier that enables viscosity-sensitivity of the BODIPY-phenyl

- **Phenyl** has mirror and planar symmetry → extrema at –90 °, 0 °
- **Methylated vinyl** has planar symmetry → maximum at –90 °
  Vinylated derivs. have no symmetry → **no** maximum at –90 °
  (*to be confirmed by transition state optimization*)