

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

S. Toliautas¹, D. Palinauskas², A. Vyšniauskas³

¹ Institute of Chemical Physics, Faculty of Physics, Vilnius University, Saulėtekio av. 9-III, 10222 Vilnius, Lithuania

² Institute of Chemistry, Faculty of Chemistry and Geosciences, Vilnius University, Naugarduko str. 24, 03225 Vilnius, Lithuania

³ Center of Physical Sciences and Technology, Saulėtekio av. 3, 10257 Vilnius, Lithuania

A widely-studied range of molecular sensors for measuring viscosity (and possibly temperature and polarity as well [1]) in microscopic environments are based on BODIPY (boron-dipyrromethene) molecule with a rotation-capable chemical group attached. The viscosity-sensitivity mainly depends on the presence and height of the moderate (50–200 meV) energy barrier between the fluorescent state of the optically-excited molecule and a non-radiative decay channel; this mechanism can be modeled, as a first approximation, by the evolution of the electronic excitation along the potential-energy curve of the lowest excited state with respect to the rotation angle [2]. However, non-trivial structure of base and rotation groups presents several challenges for such an approximation. First, a single dihedral (4-atom) angle was found to be insufficient to properly define the angle between BODIPY and rotator, both in cases where rotation group itself is asymmetric (Fig. 1A) and in cases where intrinsic symmetry is preserved but not apparent in realistic conditions, such as after the observed bending of the base in BODIPY-phenyl [2] (Fig. 1B). Second, use of asymmetric rotation groups does not result in a forced extremum at the 0° rotation angle that simplifies the model for many popular BODIPY-based sensors, such as functionally-symmetrical BODIPY-C₁₀.

The presented study, aided by quantum chemical computations based on density-functional theory, explores the potential energy surface of the lowest excited electronic state in several chemically-related BODIPY compounds. A reaction coordinate based on the average of opposite dihedral angles is shown to better estimate the actual rotation than a single dihedral. The changes in the shape of the energy surface and the emergence of the barrier upon symmetrization of a hydrocarbon-based rotation group are also investigated in more detail.

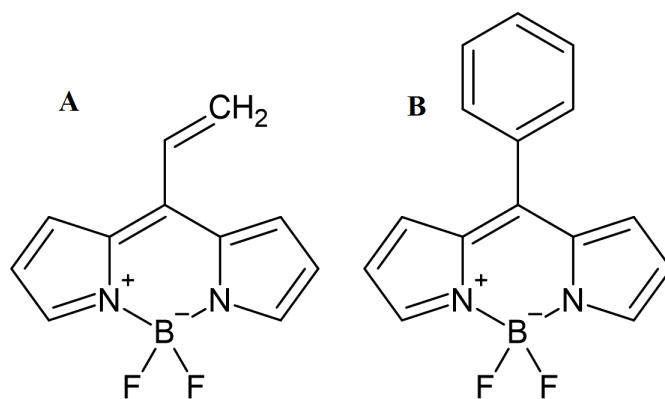


FIG. 1. Molecular structure of BODIPY compounds with asymmetric vinyl group (A) and C_{2v}-symmetric phenyl group (B)

References

- [1] K. Maleckaitė *et al.*, *Molecules* **27**, 23 (2022).
- [2] S. Toliautas *et al.*, *Chem. Eur. J.* **25**, 10342 (2019).