**Title**:

*Computational Modeling of Photophysical Phenomena: Anomalies among Kasha's Rule and Conventional Stokes Shifts*

**Abstract**:

1,6-diphenyl-1,3,5-hexatriene (DPH) dye will be studied for its hypothesized exhibition of the Suppression of Kasha's Rule (SOKR) and [1,2,3]triazolo[1,5-a]pyridinium (TOP) and [1,2,3]triazolo[1,5-a]quinolinium (TOQ) dyes will be probed for a mechanistic explanation for their Mega-Stokes shifts. All three molecules will be investigated computationally to better understand their photophysical mechanisms. Such insights are fundamental in optimizing these molecules' exceptional photophysical characteristics for applications in the expanding field of organic-based electronics. Computational chemistry offers an explicit method of studying the quantum mechanics of these photophysical phenomena: the SOKR mechanism, a novel explanation for anomalous fluorescence (light emission from high-energy excited states), and the Mega-Stokes shifts (extraordinarily large absorbance-emission energy gaps) of TOP and TOQ dyes. Both phenomena have been noted to exhibit a relationship between molecular conformation and electronic structure that can be probed by computational means. Initial success in elucidating these compounds' photophysical mechanisms through computational chemistry encourages the thorough computational investigation proposed here.

**Description of the Project**:

This project is designed to further develop the mechanistic explanations of two extraordinary photophysical phenomena: anomalous fluorescence and Mega-Stokes shifts. More specifically, DPH has been chosen to determine the role of energy gaps and molecular rotors in SOKR, and the electronic structures of TOP and TOQ dyes in the excited state will be analyzed to elucidate the cause of the molecules' Mega-Stokes shifts. In both cases, a cohesive combination of spectroscopic and computational methods is crucial for thorough analysis.

**Previous Work by Others**:

The phenomenon of anomalous fluorescence has long been recognized. Kasha's Rule[1] defines normal fluorescence based on widely observed trends in fluorescence. It states that electrons relax radiatively (i.e. emit light) only from the first excited state, and nonradiatively from all higher excited states. Though founded on an empirical basis, Kasha's Rule has found theoretical rationalization and been consistently upheld, though not universally.

Many classes of molecules have since been found that exhibit light emissions deviating from Kasha's formalism.[2] Though relatively few in number, some mechanistic explanations for these deviations have proved successful, such as twisted intramolecular charge transfer (TICT).[3] That said, the mechanisms of many fluorophores' anomalous emissions remain unknown. Boron difluorohydrazone (BODIHY) dyes' emissions from the third excited state, for instance, are not known for exhibiting the polarity sensitivity crucial to TICT mechanisms.[4] That said, many other aspects, such as the intramolecular donor-acceptor structure, are present.

TOP and TOQ salts are other examples of compounds that lack a mechanistic rationale for their unusual emissions. The energy gap between these compounds' absorbance and emission peaks, termed the Stokes shift, is exceptionally large. In most organic fluorophores, small Stokes shifts enable rapid reabsorption of emitted light, and such compounds' self-quenching makes them appear dim regardless of fluorescence yields. Large, or Mega, Stokes shifts do not allow for self-quenching, thus drastically improving net light intensity.

The Aprahamian Group synthesized both sets of compounds, the former in a collaborative project with the Liptak Group.[5] After synthesizing TOQ dyes,[6] the Aprahamian Group applied semi-empirical computational chemistry with MOPAC/MNDO to study the molecules' photophysics.[6] The results failed to represent TOP or TOQ significantly better than the Liptak Group's earlier applications of density functional theory (DFT).[5] This led to the proposition that more advanced (and unfortunately resource-intensive) methods are necessary for proper modeling.

**Previous Work by L Group Members:**

Doctor Morgan Cousins proposed SOKR following study of the anomalous fluorescence exhibited by a series of BODIHY dyes.[4] These dyes had been newly synthesized by the Aprahamian Group and were collaboratively characterized by the Liptak Group. The polarity insensitivity and viscosity sensitivity were of marked interest after the initial syntheses. Computational investigation revealed state crossings and barriers to rotation.[4] Such characteristics were distinct from contemporary mechanisms for anomalous fluorescence like TICT, so led to proposal of The Suppression of Kasha's Rule. The BODIHY project set a template with which to explore SOKR exhibition: investigations of viscosity sensitivity and polarity insensitivity followed by computational modeling.

Based on the BODIHY project, Doctor Cousins chose three molecules as potential SOKR candidates: DPH, azulene (Az), and zinc 5,10,15,20-tetraphenyl-21H,23H-porphine (Zn TPP).[7] Jacob Morris, an incoming graduate student, completed Doctor Cousins' work on Az and conducted the study of Zn TPP. Upon joining the project, I began studying DPH. Preliminary tests for SOKR were negative for Az and inconclusive for both Zn TPP and DPH.[7] Az thus moved on to computational modeling while new protocols were designed for testing the viscosity sensitivity of Zn TPP and DPH fluorescence.

TOP salts,[5] soon followed by TOQ salts,[6] were researched from a photophysical perspective by Doctor Matthew Liptak. The original computational studies were conducted with DFT using the PBE functional.[5] The choice of DFT functional followed a study of common lower level functionals in which PBE was found to be the most accurate model of absorption.[5] Conversely, PBE was the worst predictor of Stokes shifts. Computations with more complex functionals, namely PBE0 and B3LYP, were tried in an effort to find an appropriate predictor of both properties. These computations were severely limited by available computational resources. Among the obstacles were a very restrictive solvent model (particularly problematic given the compounds' noteworthy water-solubility)[5] and functionals with unsupported gradients. Since these experiments, both the solvent model and functionals have been updated in the latest version of the Liptak Group's computational chemistry package.

## Preliminary Data:

As previously noted, preliminary studies of SOKR exhibition by DPH were inconclusive.[7] Trends were inconsistent, variably increasing, decreasing, and plateauing with viscosity changes. Sample series were reproduced and retested, but a lack of reproducible results prevented conclusive analysis. Among suspected causes were poor solubility and photobleaching. The former could be remedied by changing solvent mixtures while the latter should be avoidable by adjusting instrumental parameters. To these ends, I am presently researching alternative solvent mixtures and checking the alignment of the group fluorimeter's excitation optics. It was also proposed that the all-trans conformer of DPH might be photoisomerizing. This could be verified using nuclear magnetic resonance (NMR) spectroscopy and circumvented by changing the sample preparation environment. NMR experiments have been designed to test this hypothesis using literature reports of DPH isomers' spectra for comparison.[8]

While more spectroscopic data is necessary before bringing DPH to the computational stage, the modeling of TOP and TOQ salts has already begun. This involves application of the new COSMO solvation model, as well as functionals that were previously unsupported, such as ωB97 and ωB97X. Only the most basic functionals have thus far run to completion, which, as predicted, poorly model the dyes. They were largely run for the sake of thoroughness. The more complex functionals hold more promise but need more time to process.

## Significance:

The SOKR and TOP/TOQ projects are important both academically and commercially. As a chemist, drastic changes in electronic structure resulting from photonic excitation holds promise of a new, dynamic world of photophysics. Processes initially thought forbidden, such as fluorescence from higher excited states,[1] may be possible. For example, Mega-Stokes shifts, organic high-energy photon emitters, and aggregation-induced emissions (AIE), are highly sought-after photophysical phenomena. Commercially, fluorophores with such properties are highly desirable for their efficient production of light, wide variety of colors, and ease with which their exhibitors may be implemented into electronics. The application of organic compounds in electronics is of particular interest due to their high stability, low toxicity, and low-cost relative to currently used materials.[9] Developing our understanding of DPH, TOP, and TOQ fluorescence mechanisms would expand our understanding of such properties and how to reproduce them.

## Proposed Methodology:

Procedures for investigating environmental sensitivity are adapted from previous DPH research.[7] Ethylene glycol and glycerol cocktails are to be prepared fitting a viscosity range of 20.8-620.7 cP. These viscosities correspond to mixtures ranging from 0% to 80% glycerol by volume, and the rest ethylene glycol. Viscosity was calculated by $\ln \eta_{mix} = \sum_{i=1}^{n} w_i * \ln \eta_i$, where $\eta_{mix}$ is mixture viscosity, $\eta_i$ is component viscosity, and $w_i$ is component weight fraction. The small relative polarity range of 62.8-63.7 F/m allows for isolation of viscosity sensitivity. Mixture polarity was calculated as a linear combination of component dielectrics based on percent volume. Limited solubility of DPH is resolved by dissolution in DMSO, with which ethylene glycol is stained. Consequently, about 2.5% of each mixture is DMSO. Mixtures of water and dioxane have drastically different polarities (2.3-64.17 F/m) but similar viscosities (0.89-1.19 cP), allowing for the isolation of polarity sensitivity. Spectroscopic studies will be conducted across both the viscosity and polarity gradients.

Computational analysis will be conducted using ORCA 4.0.1 software on the Vermont Advanced Computing Core's (VACC) Bluemoon cluster. All starting geometries are taken from models made in ArgusLab (Planaria Software).[7] DPH was made from scratch, the TOP monomer was made based on available crystal structure data (CCDC number 841443),[5] and the other TOP and TOQ dyes were built using the TOP monomer as a template. All structures are to be optimized via density functional theory (DFT) geometry optimization with a variety of functionals. These include GGA functionals: BLYP and PBE, hybrid-GGA functionals: B3LYP and PBE0, and range-separated hybrid functionals: ωB97 and ωB97X. DPH will also be modeled with a meta-GGA functional: TPSS, a hybrid meta-GGA functional: TPSSh, and a double-hybrid functional: B2PLYP. All use a triple-zeta basis set with tight SCF convergence. TOP and TOQ calculations apply the COSMO continuum solvation model to factor in solvent effects. Solvents were chosen according to experimental data: water for the TOP compounds,[5] methanol for the TOQ monomer,[6] and acetonitrile for the TOQ dimer.[6] Time-dependent DFT (TDDFT) calculations model excited states and energy levels. In all cases, the RIJCOSX approximation can be used to decrease resource-demand. The orca_mapspc utility program allows for construction of absorbance spectra.

All necessary instruments are available on campus. The L Research Laboratory operates a Cary 100 Bio spectrophotometer for ultraviolet-visible light absorption spectroscopy and a Photon Technology International QuantaMaster 4 spectrofluorometer for fluorescence spectroscopy. The University of Vermont also manages two NMR spectrometers which are available for research. Spectra are processed with Cary WinUV Scan, FelixGX 4.2.2, and TopSpin 3.2 software, respectively. The VACC's Bluemoon cluster is available to registered researchers. Chemical samples have already been purchased with grant money for the SOKR project. The project is not expected to incur any new costs.

The project is planned to finish a few months into the Spring 2020 semester. Experimental studies of DPH's exhibition of SOKR should be complete by the end of the summer and computational studies will hopefully be complete by the end of the Fall 2019 semester. Setting a deadline for computational experiments is challenging due to the expansive range of models available. At the very least, a variety of DFT functionals must be tested, but CCSD and CASSCF methods will be resorted to if DFT fails to provide satisfying models. Spring 2020 would be spent analyzing data and composing the thesis dissertation. This schedule has the added benefit of providing winter break should the computations take longer than expected. About two months of analysis followed by another of thesis writing and presentation preparation would set the thesis defense towards the end of March or beginning of April.

**References**:

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