

Minding the Gap: Synthetic Strategies for Tuning the Energy Gap in Conjugated Molecules

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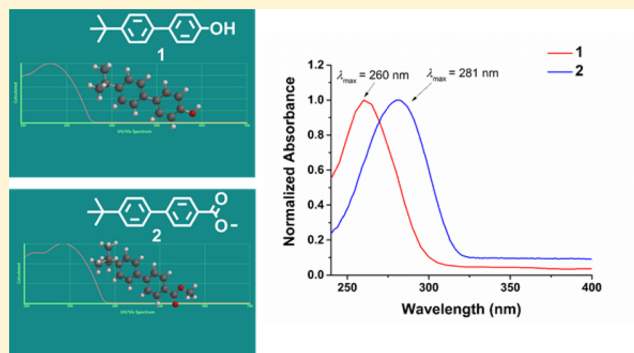
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Supporting Information

ABSTRACT: While structure–property relationships are commonly developed in applications of physical organic chemistry to real-world problems at the graduate level, they have not been generally emphasized in the undergraduate chemistry curriculum. For instance, the ability to modify the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in π -conjugated small molecules and polymers is of particular interest in the fields of polymer chemistry and materials science, where small-gap systems can function as semiconductors in electronic devices. In order to demonstrate a general strategy for tuning the HOMO–LUMO energy gap for π -conjugated materials, a new experiment was designed for the

undergraduate organic laboratory course that combines synthesis with theoretical calculations for π -conjugated biphenyl systems with differing electronic properties to generate a simple structure–property study of functional group substitution on the biphenyl core. The synthesis of electron-rich and electron-poor biphenyl compounds was accomplished by students with a modified procedure from the literature that uses green Suzuki conditions to yield 4'-(*tert*-butyl)-[1,1'-biphenyl]-4-ol (**1**) and methyl 4'-(*tert*-butyl)-[1,1'-biphenyl]-4-carboxylate (**2**) with average yields of ~50% and ~60%, respectively. The students characterized their products with TLC, NMR, IR, and UV–vis (from a representative sample) spectroscopies. A comparison of the UV–vis absorption spectra from density functional theory calculations and experiment showed how a π -conjugated system's HOMO–LUMO gap was tunable with structural modifications to the core, which illustrated how physical organic principles could be used to understand the electronic properties of a π -conjugated system.

KEYWORDS: Upper-Division Undergraduate, Organic Chemistry, Interdisciplinary/Multidisciplinary, Inquiry-Based/Discovery Learning, Materials Science, Molecular Properties/Structure, Spectroscopy, Synthesis, NMR Spectroscopy, IR Spectroscopy



INTRODUCTION

As the world's demand for cost-effective, flexible, and portable electronic devices increases, the field of organic materials is developing strategies to improve the efficiency of solar cells, organic light-emitting diodes and field-effect transistors.^{1–3}

Through the combination of computation and synthesis, structure–property studies for a class of materials allows for a fundamental understanding of how to synthetically modify the π -conjugated core to tune its electronic properties for a specific electronic device.^{4,5} Structure–property relationships have been successfully developed for a variety of conjugated materials, including recent studies with linear *N*-heteroacenes.⁶ In these studies, theoretical calculations were performed with density functional theory (DFT) using the B3LYP functional at the 6-311G** level of theory (where B3LYP is the functional and 6-311G** is the basis set used).⁷ DFT is a cost-effective and moderately accurate computational method, especially for systems comprised of main group elements.⁸ Consequently, DFT is the most commonly used method for calculating the

conformational and electronic properties of π -conjugated systems in the ground and excited states,^{7,9} where the energy gap of π -conjugated small molecules or the energy gap of a polymer can be calculated from the electronic properties of the ground state.

The experiment is designed for an advanced undergraduate laboratory in organic chemistry and incorporates organic synthesis and aspects of computational chemistry to develop a basic structure–property study of a π -conjugated small molecule. The present experiment's goal is to demonstrate how substituents on a π -conjugated core can affect the electronic and optical properties of a conjugated system. Students were expected to develop and adapt their own synthetic procedure from primary literature to synthesize both an electron-rich and an electron-poor biphenyl compound. Then students purified

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and characterized their products with a variety of techniques. Finally, the students were required to write a formal lab report in the form of an ACS-style manuscript.

There are limited reports of the introduction of structure–property relationships into the undergraduate organic laboratory curriculum,^{10,11} although the method is commonly used in materials science and physical organic chemistry laboratories. The underlying pedagogical goal of this undergraduate laboratory experiment is 3-fold. First, students must adapt two different green synthetic approaches to Suzuki chemistry to synthesize two electronically different biphenyl compounds. Second, students must develop a purification procedure based on which synthetic route they chose to purify each compound. Third, students must characterize each compound with spectroscopic techniques and compare representative class data from UV–vis spectroscopy to a representative class theoretical calculation to understand how the HOMO–LUMO gap of a conjugated system is changed with structural modifications to a biphenyl core.

In this experiment, students were introduced to theoretical calculations performed with Spartan '14 software, which was used to predict the HOMO–LUMO gaps and orbital energy levels for electron-rich and electron-poor biphenyl compounds. Then, students synthesized both compounds with different variations of green Suzuki cross-coupling chemistry, which is a powerful tool for synthesizing π -conjugated small molecules and polymers.^{5,12–14} They analyzed their products with TLC, ¹H NMR and IR spectroscopies. Finally, students obtained representative UV–vis absorption spectra from the purest products, and they calculated the optical HOMO–LUMO gap to compare with the class's theoretical calculations.

EXPERIMENT

Students worked individually to synthesize each of the target biphenyl compounds. Depending on the level of skill of the student, the experiment requires three to four 2 h 40 min class periods. It took an additional class period to obtain the necessary characterization. The class was given primary literature references to aid in their understanding of the synthesis and theoretical calculations and were required to consult with the course instructor about the prelab notebook assignment. For the prelab assignments, students were given only a chemical reaction (based upon the primary literature they had access to) and the scale of the reaction's starting materials. They were expected to calculate the amounts of all reagents and theoretical yields of products, and record safety precautions, as well as keep a detailed flowchart in their notebooks.^{15–17} Detailed synthetic procedures for the synthesis and purification of both target compounds 4'-(*tert*-butyl)-[1,1'-biphenyl]-4-ol (**1**) and methyl 4'-(*tert*-butyl)-[1,1'-biphenyl]-4-carboxylate (**2**) (the synthesis of an electron-rich and electron-poor biphenyl compound, as shown in Scheme 1) can be found in the Supporting Information.

HAZARDS

The students were required to include safety precautions for all reagents (available from the MSDS at Sigma-Aldrich) used in the syntheses of the products as part of their prelab assignments in their lab notebooks. Goggles, lab aprons or lab coats, and appropriate nitrile gloves were worn at all times during the experiment, and all synthetic work was performed in fume hoods. In particular, for the synthesis of **1**, sodium carbonate is

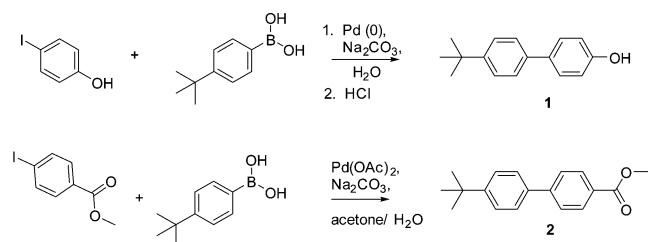
irritating to the eyes, respiratory system, and skin. The compounds 4-iodophenol and 4-*tert*-butylphenylboronic acid are skin irritants and harmful if inhaled. Methanol is highly flammable and toxic if swallowed. Hydrochloric acid can cause burns and is irritating to the respiratory system. All palladium waste was stored separately and disposed of in accordance with EPA guidelines. When working with palladium, care was taken to not let the dry solids come into direct contact with alcoholic solvents (e.g., methanol), which can be pyrophoric. All palladium waste was kept separate from organic waste and stored with water to prevent solids from drying out. For the synthesis of **2**, all solvents used are flammable and irritants to the skin, eyes, and respiratory system. All reactions should be carried out in the absence of an open flame. For the purification of **2**, *n*-hexane is a neurotoxin through inhalation and an irritant, so all chromatography employing *n*-hexane in the mobile phase was performed in the fume hoods. Based on other biphenyl compounds in the literature, compounds **1** and **2** are suspected irritants. The solvent used in ¹H NMR analysis was CDCl₃, which is harmful when inhaled or in contact with skin and is a known carcinogen. In the UV–vis absorption spectroscopy, dichloromethane was used as a solvent, which is known to be harmful and a carcinogen.

RESULTS AND DISCUSSION

This experiment was performed in an advanced organic undergraduate laboratory, in which the class met for 2 h 40 min every week and it was composed of 17 students that had each completed the two-semester introductory organic chemistry sequence. The students had prior knowledge about TLC, NMR, and IR spectroscopies and column chromatography. Most students had a basic understanding of UV–vis absorption spectroscopy theory and instrumentation, but this was revisited in the prelab lecture prior to starting the experiment, with particular emphasis on optical HOMO–LUMO gap determination. The students had no prior knowledge of computational chemistry or experience with Spartan '14 software. Due to licensing constraints with the software, the calculations were set up as a class demonstration and allowed to run throughout the class period, while the students performed the syntheses. Theoretical calculations were performed with Spartan '14 using density functional theory at the B3LYP/6-311G* level of theory from the PM3 starting geometry. This calculation was the most time-economical and it gave the best agreement between theoretical and experimentally determined HOMO–LUMO gaps when compared with *ab initio* HF calculations.

The synthesis of **1** via a Suzuki Cross-Coupling reaction proceeded without any side reactions, and all of the students produced pure products (determined from NMR analysis) with a range of yields from 21 to 70% after crystallization from methanol (Scheme 1). All of the student products were pure by ¹H NMR (compared with known compounds in the literature^{18,19}) and TLC analyses. The synthesis and purification of **2** were more challenging for the students. Approximately, 13 of the 17 students obtained the pure product in a range of yields from 21 to 92% after purification of the product through silica gel column chromatography. The student product ¹H NMR spectra were compared with the literature for this particular compound.^{15,20} Some students that completed the experiment obtained a mixture of the product with methyl 4-iodobenzoate (which coeluted with the product during column chromatography and was evident in the

Scheme 1. Synthesis of 1 and 2 via Suzuki Coupling Chemistry



aromatic region of the ^1H NMR spectrum). This suggests that the reaction did not proceed to completion, which is due to temperature fluctuations during the reaction. It has been noted in the literature and that the reaction is very sensitive to temperature and should be maintained between 40 and 45 $^\circ\text{C}$ for 60 min.¹⁵ When the temperature was maintained within this range, there was no trace of starting material by TLC and NMR analyses (as shown in the [Supporting Information](#)).

The students analyzed their products by running their own TLC and IR spectroscopic analysis in the lab. They prepared their individual samples for ^1H NMR analysis, which was run by the instructor, and the data were returned to the students for analysis.

Due to time constraints and product purity considerations, a representative UV–vis spectrum for each of the purest products was obtained in a solution of dichloromethane. Ideally, each student should obtain their own UV–vis spectral data after obtaining ^1H NMR spectral data for their products; this allows each student to reflect upon the purity of their compounds (see [Supporting Information](#)).

When comparing the two products in [Figure 1](#), the students observed a bathochromic shift in the absorption maximum of 21 nm for compound 2 (see [Supporting Information](#) for discussion). The students prepared lab reports after the experiment, and they were asked to consider how substituents changed the HOMO–LUMO gap in a π -conjugated material. As the lab reports suggested, the weaker students in the course did not make clear connections to how the underlying molecular orbitals in a structure can affect the optical properties of a π -conjugated system. Approximately one-third of the students understood that the electronics of the molecular

orbitals changed with the electronically different substituents, which affected the HOMO–LUMO gap (as evident in the class demonstration of the UV–vis absorption spectra from calculations with Spartan '14 and from experiment; see [Table 1](#)). Some students even made the connection that computation

Table 1. Experimental and Theoretical HOMO-LUMO Gaps for 1 and 2

Compound	ΔE_{calc} , eV (λ_{max} , nm) ^a	ΔE_{exp} , eV (λ_{max} , nm) ^b
1	4.71 (263)	4.77 (260)
2	4.35 (285)	4.41 (281)
4-(<i>tert</i> -butyl)-1,1'-biphenyl	5.0 (248)	^c

^aThe HOMO–LUMO gap (ΔE_{calc}) and corresponding λ_{max} were calculated using density functional theory at the B3LYP/6-311G* level of theory with Spartan '14. ^bThe HOMO–LUMO gap (ΔE_{exp}) and corresponding λ_{max} were experimentally determined from the UV–vis absorption spectrum in dichloromethane solution. ^cData not available.

is a powerful complement to synthesis that can help in designing new materials for applications outside of electronic materials (e.g., pharmaceutical applications).

CONCLUSIONS

Students synthesized two electronically different biphenyl compounds through aqueous Suzuki chemistry. While most students synthesized 1 in moderate yields with ease of purification, the synthesis of compound 2 was more challenging and approximately two-thirds of the students successfully synthesized the pure product. This issue can be addressed by monitoring the reaction temperature carefully.

This experiment provided an introduction to developing structure–property relationships with computation and experiment for electronic materials. Prior to the experiment, the students had limited knowledge of computational chemistry and had to learn how to build molecules and perform theoretical calculations using the Spartan '14 software. After the experiment, the students were asked to compare the effect of a weak electron-donating group (such as a hydroxyl substituent) with a stronger π -accepting group (such as an ester) to gain a deeper understanding of how structural modifications to a π -conjugated core can alter the material's HOMO–LUMO gap.

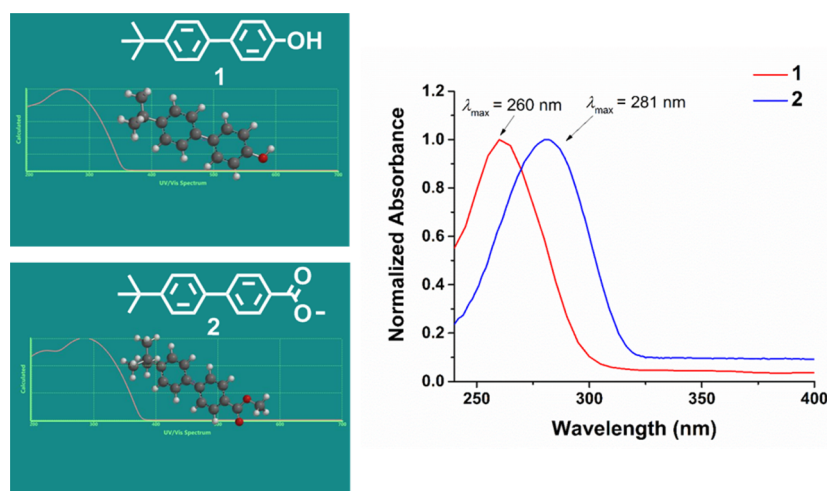


Figure 1. Results from experiment and calculation for the UV–vis absorption spectra for compounds 1 and 2.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.5b00916](https://doi.org/10.1021/acs.jchemed.5b00916).

Experimental spectral data for all products and the theoretically predicted Spartan '14 spectra with energy diagrams and details of prelab lectures (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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