# The Applications and Properties of Hydantoin as a Photoswitch

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## 1. RESEARCH STATEMENT

For novice learners in nanotechnology who are interested in the basics and applications of photoswitches such as hydantoin, the following paper on the properties and applications of hydantoin as a photoswitch serves as an introduction to the fundamental role hydantoin plays as a photoswitch as well as the broader applications of it in the field of nanotechnology.

## 2. ABSTRACT

Photoswitches are rapidly advancing technologies that can have a large impact on the future of solar energy, protein storage and the controlled storage, release and conversion of many different types of energy. Due to their complexity and large variety in viable molecules, a strong foundational understanding of the properties of a photoswitch as well as the applications of a photoswitch molecule—in this case, the hydantoin molecule—is key to be able to contribute to this fast-paced technological advancement. We examined several variants of hydantoin as well as their applications as photoswitches by examining four key properties: modified substituents, dipole moment, excitation energy and maximum absorption wavelength. We procured a simple cause-effect relationship between the modified substituents and the maximum absorption wavelength and proposed an efficient hydantoin molecule that would potentially reap a high maximum absorption wavelength, preferably within the range of visible light. The hydantoin molecule with only the R3 substrate being modified with a phenyl ring (C6H5) produced the highest maximum absorption wavelength of 153.7108 nm and the lowest dipole moment of 1.5561 debyes. We proposed and developed a hydantoin with a larger organic molecule as the R3 substrate (octahydrocoronene) which produced a maximum absorption wavelength of 210.7305 which was 1.1561 off our predicted value based on our data. This proves a semi-linear increase in the maximum absorption wavelength of hydantoin as the amount of carbon structure increases.

**Keywords:** Light, hydantoin, Computational Chemistry, photoswitch

## 3. INTRODUCTION

Photoswitches are fundamentally important innovations in nanoscience. These molecules detect light at a distinct wavelength and therefore can be used for various purposes in storing and manipulating energy, proving them to be indispensable resources. The most common molecule used as a photoswitch is an organic molecule called azobenzene (figure 1); when this molecule is hit by a certain wavelength of light, it undergoes a process called photoisomerization. Azobenzene photoisomerization is the process of changing structures, or isomers, of an azobenzene molecule; for this specific molecule, it switches to a trans isomer when subjected to wavelenghts from 300-400 nm and to a cis isomer when subjected to wavelengths greater than 400 nm.

Photoswitch molecules are known to harness two types of energy, light energy and chemical energy. Light energy is a form of kinetic energy; it's the energy carried along the various waves of light in the electromagnetic spectrum. As with the azobenzene molecule, the amount of light energy harnessed by the photoswitch molecule is dependent on the "trigger wavelengths" of the molecule and the subsequent isomer formation. The transformation occurring during photoisomerization breaks bonds within the molecule and stores the energy created from that process into the formed isomer. This energy is known as chemical energy, which is a form of potential energy. The conversion and storage of light energy to chemical energy within photoswitches is key to their versatility and myriad of functionality.

Though azobenzene is the "go-to" when considering molecules as photoswitches, other molecules, such as hydantoin (as shown in figure 2), and its many variants, are viable structures to undergo photoisomerization.

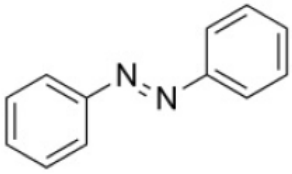


Figure 1. The trans isomer of a azobenzene photoswitch molecule.

The hydantoin molecule contains three substituents, known as ligands, as denoted by R1, R2, and R3. These ligands can be altered to construct different forms of the hydantoin molecule, ultimately changing the intrinsic properties of the molecule. Though the primary use for such molecules is as a pharmaceutical, hydantoin variants can effectively be used as photoswitches. Similar to the azobenzene molecule, the hydantoin molecule undergoes photoisomerization when hit by a specific wavelength of light. A widely used hydantoin, aryldenehydantoin, switches from an E isomer to a Z isomer (as shown in figure 3) when subjected to specific forms of light radiation, denoted as hv.

In this paper, we examine the application of hydantoin as a photoswitch through various computational

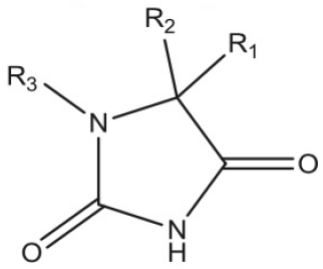


Figure 2. Hydantoin molecule where R1, R2 and R3 denote the different, changable substituents

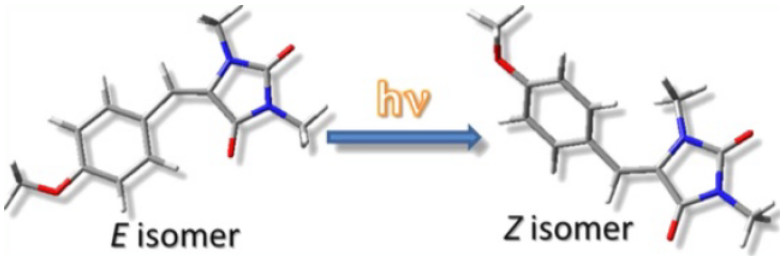


Figure 3. Isomerization of hydantoin molecule. Shift from E isomer to Z isomer when subjected to light radiation.

processes. A few properties we analyzed were the maximum light absorption wavelength, excitation energy and dipole moment, which are elaborated on in the results section. The analyses in this paper help provide a strong foundation of the properties of hydantoin as a photoswitch. The trends and concepts learned from this paper can also provide a deeper understanding of hydantoin's applications as a photoswitch, which provide key insight into the benefits of efficient energy storage provided by such molecules.

## 4. RESULTS

We ran geometry optimization calculations and excitation energy/UV-Vis calculations on a computational chemistry server for 5 different variants of hydantoin, where each variant contained a different combination of substituents R1, R2, and R3 (as shown in table 1).

Dipole moment is the measure of the polarity of a molecule; this can be measured through the separation

Table 1. Excitation energy, dipole moment, maximum absorption wavelength and substituent contents for 5 different hydantoin variants.

| Molecule Number | R1 | R2 | R3 | Dipole Moment (debyes) | Excitation Energy (eV) | Maximum Absorption Wavelength (nm) |
|---|---|---|---|---|---|---|
| 1 | H | H | H | 2.4341 | 5.8756 | 135.0896 |
| 2 | CH2CH2CH2CH3 | H | H | 2.4759 | 5.8841 | 137.9845 |
| 3 | C(CH3)3 | C(CH3)3 | H | 2.3697 | 5.9204 | 139.0570 |
| 4 | CH3 | CH3 | CH3 | 2.5792 | 5.9012 | 141.4623 |
| 5 | H | H | C6H5 | 1.5561 | 5.8528 | 153.7108 |

of charge of ionic or covalent bonds. Excitation energy is the energy required to supplement a system so that it results in an alteration from a lower, preferably ground state, level to a higher order energy level. Maximum absorption wavelength is the light wavelength at which a molecule absorbs the most amount of light; this data is taken from a UV-Vis graph (as shown in figure 4). Knowledge of the trends and influence of each of the specified properties is key to developing the holistic knowledge base of hydantoin photoswitches.

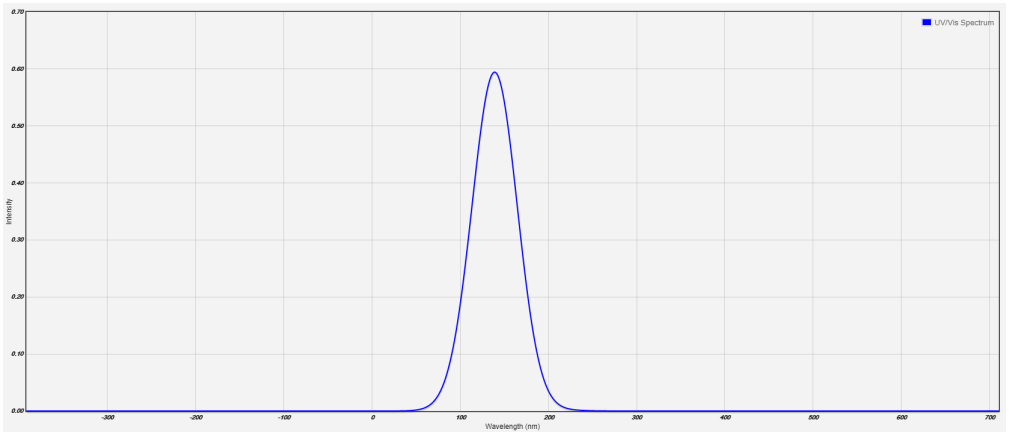


Figure 4. Example of UV-Vis spectrum for Molecule 1. Shows absorption proportion as compared to wavelength.

## 5. ANALYSIS AND DISCUSSION

The purpose of this paper was to explore and analyze the application of hydantoin as a photoswitch, therefore we applied the data from the calculations to propose a viable hydantoin molecule to act as an efficient photoswitch. Making sure we apply these data to the larger context of viable hydantoin molecules, we decided which trends and properties were most influential to maximizing the maximum absorption wavelength to potentially reach the visible light range of 400-700nm. In addition, to give structure and formality to our analysis, we decided that Molecule 1, where all 3 substituents are individual hydrogen atoms, would act as a "control" variant of hydantoin. All the properties of each other hydantoin variant were compared to those of Molecule 1 by displaying the positive or negative change that occurs (as shown in table 2).

When first looking at the table, it seemed that there is a moderate inverse correlation between dipole moment and maximum absorption wavelength. Though there were some "outliers" to this fairly restrictive model, we generally concluded that the dipole moment tended to decrease as the maximum absorption wavelength increased. Another key component in our construction of an "ideal" hydantoin is the amount of modified substrates. For the scope of this paper, we defined a modified substrate as one that is not a single hydrogen atom, as a single

Table 2. Relative change in the value of each property for hydantoin Molecules 2-5 as compared to those of Molecule 1

| **Molecule Number** | **Change in Dipole Moment (debyes)** | **Change in Excitation Energy (eV)** | **Change in Maximum Absorption Wavelength (nm)** |
|---|---|---|---|
| 2 | +0.0418 | +0.0085 | +2.89495 |
| 3 | -0.0644 | +0.0448 | +3.9674 |
| 4 | +0.1451 | +0.02562 | +6.3727 |
| 5 | -0.878 | -0.0228 | +18.6212 |

hydrogen atom is our "control" standard. The molecules with 1-2 modified substrates seemed to have a greater impact on maximum absorption wavelength per substrate than the molecules with 3 or 0 modified substrates.

Using the large-scale observations made in the aforementioned paragraph, developed the composition of each substrate of our proposed molecule. In this process, each substrate was thought of as independent of each other as they were structured differently; therefore assumed dependency may have led to faulty calculations. Of our 5 calculated variants, Molecule 5 had the highest maximum absorption wavelength of 153.7108 nm. This molecule only contained 1 modified substrate, an organic compound known as a phenyl ring (as shown in figure 5). Since we viewed each substrate independently, we focused on the composition of the R3 substrate with the addition of more phenyl groups to potentially increase the maximum absorption wavelength to 400-700nm. A stable organic compound with a similar composition ratio to a phenyl group is octahydrocoronene (formula C24H20), since this was known to be a stable organic compound with a similar structure, it was safe to assume this molecule, as the R3 substituent, would have a extended positive impact on the maximum absorption wavelength. The proposed molecule (as shown in figure 5) only contained one "modified substrate", R3, with the octahydrocoronene molecule.

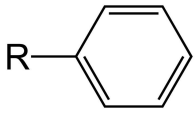


Figure 5. Phenyl ring diagram where R is the atom which the compound is attached to.

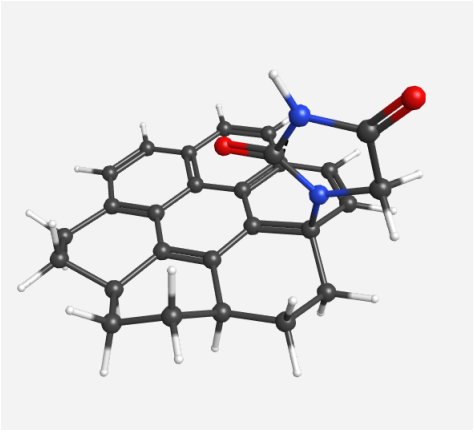

Figure 6. Proposed molecule with octahydrocoronene (C24H20) molecule as the R3 substrate.

Since the ratio of molecules from octahydrocoronene to a phenyl ring is 4:1, our predicted maximum wavelength, using the values from table 2, was:

$$(18.6212 * 4) + 135.0896 = 209.5744nm \tag{1}$$

Going through the same steps as with calculating the first 5 variants of the hydantoin molecule, we calculated the "geometry optimization" and the "excited state and UV-Vis" for our proposed molecule. Since we were only focusing on how the addition of carbon structures to the R3 substituent affected the maximum absorption wavelength of the hydantoin variant, we took a close look at the UV-Vis spectrum for the proposed molecule (as shown in figure 7) to extract our desired value. According to the UV-Vis spectra for our proposed molecule, the maximum absorption wavelength is approximately 210.7305 nm, which is very close to our predicted value. Though this wavelength did not reach the visible light spectrum (400-700 nm), its similarity to our prediction presents another key finding. The underlying cause for this correlation may be circumstantial, but if not, the correlation for the addition of additional carbon structures to the R3 substituent can be classified as linear or semi-linear.

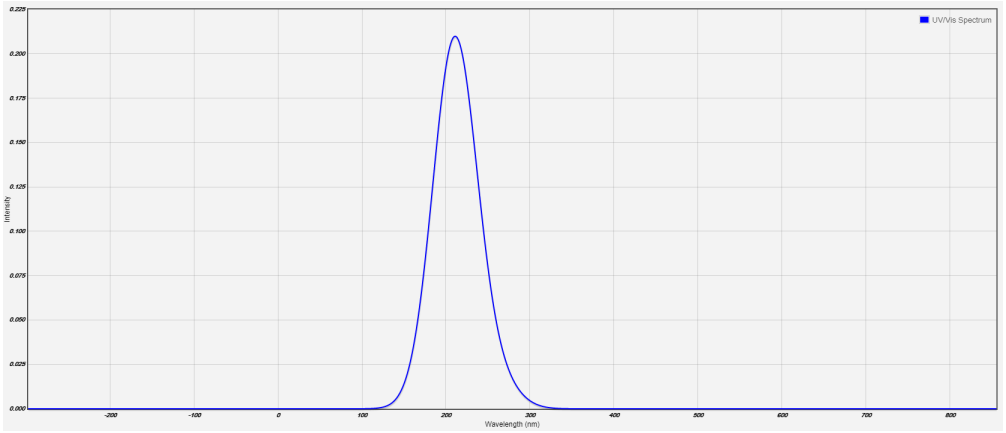


Figure 7. The UV-Vis spectrum showing the maximum absorption wavelength for our proposed molecule.

## 6. CONCLUSION

Undergoing this computational process allowed us to better understand and convey the properties and applications of hydantoin. The purpose of this paper was to research and explore the various properties and applications of hydantoin as a photoswitch. We experimented with various substitiuents and used those data to fairly accurately predict the maximum absorption wavelength of a proposed molecule that would have a higher maximum absorption wavelength than any of our 5 starting molecules. Using an extention to a phenyl group, with the same ratio of atoms, we developed an octahydrocoronene molecule as our R3 substituent. Using the data from one of our molecules, we predicted that the maximum absorption wavelength of our proposed molecule would be approximately 209.5744 nm. After calculating the properties for the proposed molecule and extracting the data from the UV-Vis spectrum, we discovered our prediction was fairly close to the actual value, 210.7305 nm, leading us to believe that a model-able linear correlation for max. abs. wavelength exists. We wanted to maximize the absorption wavelength of our photoswitch to ensure a more absorbent, and consequently, efficient hydantoin photoswitch. With a more efficient photoswitch, the hydantoin molecule can broaden its applications from those of protein storage and light energy detection to solar energy storage in photovoltaic cells and even everyday use as a temporary fuel cell. Our process was restricted by a limited time frame and a fairly small sample group to gain data and properties from. Elaboration on the calculations conducted in this paper is advised to gain a greater understanding of the applications and properties of hydantoin photoswitches.

## 7. METHODS

The primary research and data collection in this paper was done through the NCSSM Computational Chemistry server at chemistry.ncssm.edu. For each variant of hydantoin, we followed a step-by-step process to produce accurate calculations for all the desired properties. First, when in the server, we created a new job. While in that job, we would build the hydantoin molecule; this can be done either by searching it up by name in the computational chemistry server or by building it manually. After the hydantoin molecule is built, we built

the substrates upon the pre-built ligands. Once the construction of the molecule was finished, we mechanically optimized the molecule in order for calculations to run smoothly and accurately. The first calculation we ran for each hydantoin variant was "geometry optimization."

Once the geometry optimization calculation concluded, we ran an "excited state and UV-Vis" calculation on the same job. When running this calculation, we had to change the theory we used from the default theory to "TD-HF" to align with our desired results. The results from both these calculations were presented in distinct sections in the completed job with different calculated properties within each section. For this paper, we focused on only 4 of such properties: substituents (R1, R2, R3), dipole moment, excitation energy and maximum absorption wavelength.

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