

# Comparison of Isomeric Aryldibenzopyrylium Salts as Highly Conjugated Planar Dyes

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## Abstract

Planar conjugated organic compounds can be incorporated into a variety of applications due to their unique optical properties. One such class of these compounds contains the pyrylium unit, which is capable of reversible pH-driven conformational changes. This project focuses on the synthesis of novel aryldibenzopyrylium dyes with optimized pH sensitivity and the ability to reversibly alter their conformations, thus producing variable optical properties. We set out to synthesize a new class of isomeric compounds, which incorporate a doubly benzannulated pyrylium unit in each structure, to determine how the molecular shape impacted the optical properties. These properties can be studied using UV-vis and fluorescence emission detection techniques. These analyses allow for a deeper understanding of the electronic properties of these molecules and how both the conjugation path length and structural motifs alter these properties. This work has not only yielded an entirely new class of pH-sensitive fluorescent molecules but has contributed to the constantly evolving understanding of electronic activity in conjugated pathways.

## Isomeric Compounds

Isomeric compounds are molecules that consist of the same number and types of atoms, but whose atoms are arranged differently. This research compares analogs of two isomeric compounds, xanthone and 6H-benzo[c]chromen-6-one (Figure 1).

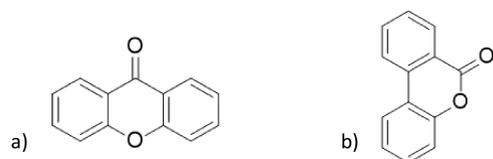


Figure 1. Isomeric aryldibenzo motifs incorporated in all newly synthesized compounds. a) Xanthone b) 6H-benzo[c]chromen-6-one

These compounds are not only isomeric but are also conjugated. Conjugation refers to the alternating double bonds throughout the molecules' structures that give rise to overlapping pi-orbitals. This overlap allows electrons to be easily shared between these orbitals. However, this is only possible if the molecule adopts a planar conformation. If the molecule is in a non-planar conformation, the pi-orbitals cannot sufficiently overlap, and thus there is no sharing of electrons between the orbitals. Because of this difference in electronic activity and propagation, conjugation has drastic effects on the optical and spectroscopic properties of a molecule. These differences in characteristics between the planar and non-planar states are utilized in order to produce the reversible nature of our newly synthesized dyes.

## 9-arylxanthylum Salts vs. 6-aryldibenzo[b,d]pyrylium Salts

While 9-arylxanthylum salts, containing the xanthone motif, are well characterized in the literature, their isomeric counterparts, 6-aryldibenzo[b,d]pyrylium salts, containing the 6H-benzo[c]chromen-6-one motif, are rare. We synthesized novel 6-aryldibenzo[b,d]pyrylium salts, as well as their 9-arylxanthylum analogs, in order to explore their differences in spectroscopic properties and conjugation path length (Figure 4). In total, seven 6-aryldibenzo[b,d]pyrylium salts and their xanthylum analogs were synthesized (Figure 2).

## Conformational Reversibility with Changes in pH

Once fully synthesized the pyrylium salts display brilliant colors, an unusual characteristic for organic compounds. However, the direct synthetic precursors of these salts are white solids that dissolve colorlessly in solution. These precursors are alcohols that contain a stereocenter at the carbon attached to the R group.

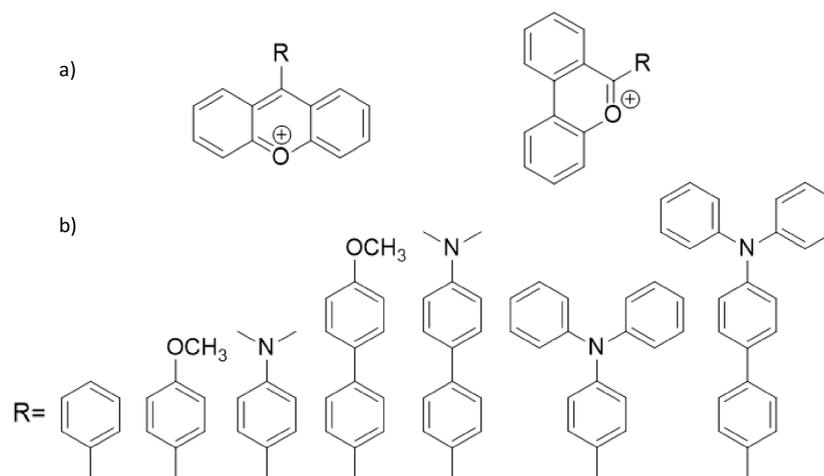


Figure 2. a) The pyrylium motifs present in the synthesized salts. b) The varying R groups that were incorporated with the motifs seen in a. The organic cations were complexed with either ClO<sub>4</sub> or BF<sub>4</sub> anions.

This forces the molecules into non-planar conformations. The precipitation reaction that results in the formation of the salt utilizes acid-catalyzed elimination chemistry to reduce the alcohol functional group into a double bond. The elimination reaction is responsible for creating the positive charge on the organic half of the pyrylium salt and for forcing the molecule into a planar conformation.

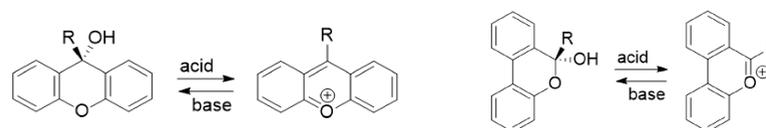


Figure 3. Reversible acid-catalyzed elimination chemistry for both the xanthone and 6H-benzo[c]chromen-6-one motifs.

We capitalize on the reversible nature of elimination chemistry to make our newly synthesized salts useful as reversible dyes. Addition of acid favors the elimination reaction, resulting in brightly colored solutions and solids, but addition of base to one of these solutions restores the alcohol functional group and dissipates the color (Figures 3 and 5). This simple change in pH readily converts the compound of interest between its salt and alcohol forms, changing its optical properties as it does. Our molecules can undergo several rounds of reversibility before the effects begin to be less apparent.

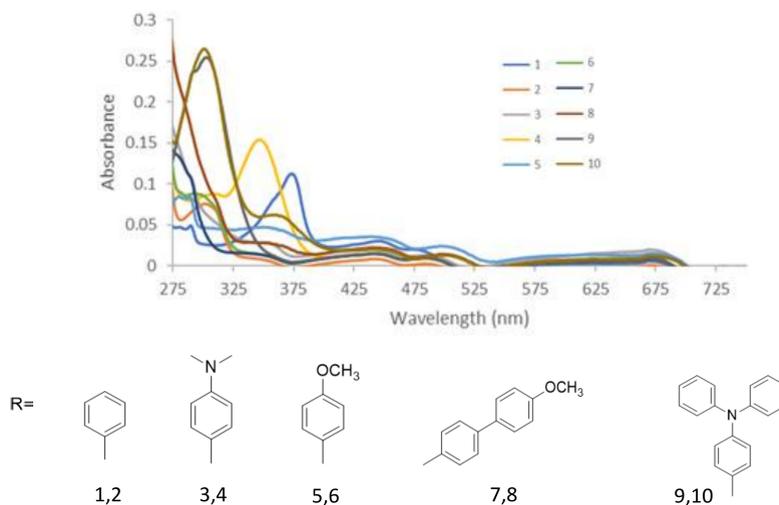


Figure 4. UV-Vis spectra of ten pyrylium salts at a concentration of 0.010 mM in CH<sub>3</sub>CN. The odd numbers represent the corresponding R groups attached to the xanthylum motif. The even numbers represent the corresponding R groups attached to the 6-aryldibenzo[b,d]pyrylium motif.

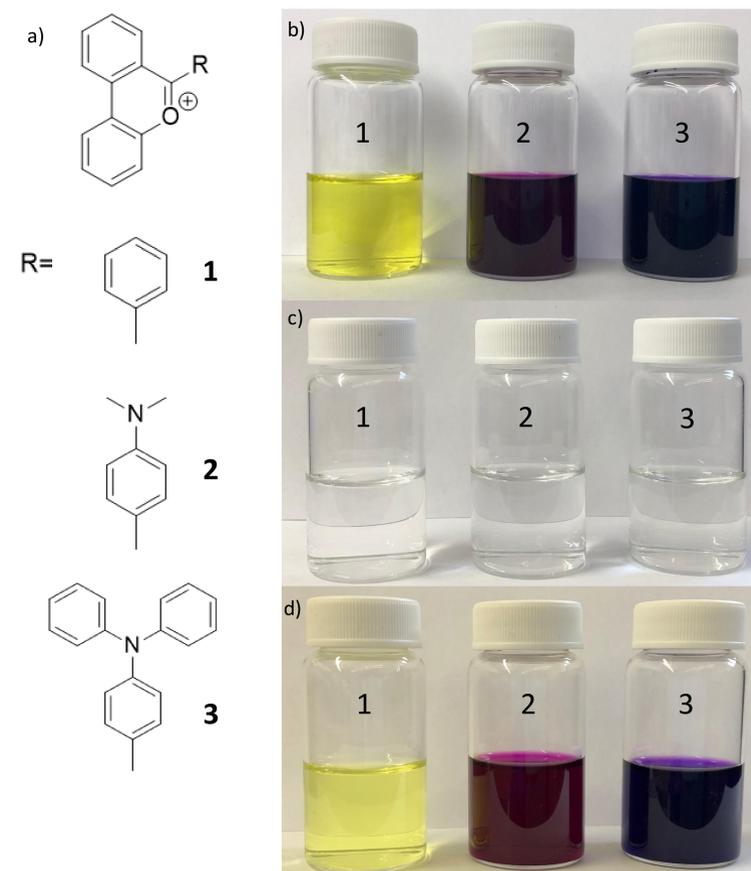


Figure 5. a) The pyrylium salts corresponding to the vials in b, c, and d. b) From left to right, compound 1 (0.48 mM), compound 2 (0.49 mM), and compound 3 (0.49 mM) in 10 mL of CH<sub>3</sub>CN. c) Solutions in b after addition of 10  $\mu$ L (0.072 mmol) of TEA to 1 and 90  $\mu$ L (0.645 mmol) of TEA to 2-3. e) Solutions in c after addition of 200  $\mu$ L (2.61 mmol) of TFA to each.

## Conclusions

Figure 5 shows our newly synthesized 6H-benzo[c]chromen-6-one-based pyrylium salts do indeed readily undergo interconversion between their salt and alcohol states. The disappearance of color in Figure 5c represents the conversion to the non-planar alcohol form of the compound, thus disrupting conjugation and resulting in no color. Figure 5d demonstrates the resurrection of color and with it, the elimination reaction that restores the pyrylium salt. This demonstration proves these molecules have the ability to reversibly interconvert between their planar and non-planar states, varying their optical properties as they do so. This characteristic makes them highly applicable as pH-sensitive dyes.

## References

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