

A Simple Visualization of Double Bond Properties: Chemical Reactivity and UV Fluorescence

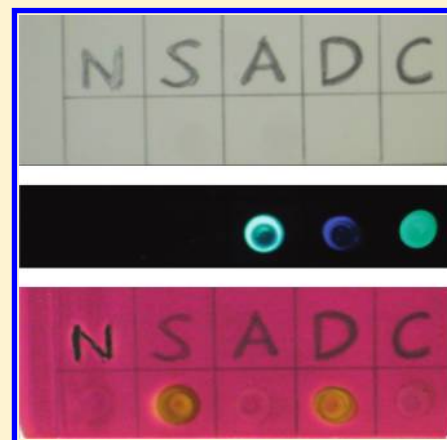
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ABSTRACT: A simple, easily visualized thin-layer chromatography (TLC) staining experiment is presented that highlights the difference in reactivity between aromatic double bonds and nonaromatic double bonds. Although the stability of aromatic systems is a major theme in organic chemistry, the concept is rarely reinforced “visually” in the undergraduate curriculum. With the use of a TLC plate to immobilize a range of unsaturated hydrocarbons, their UV fluorescence properties and their susceptibility to oxidation, using a permanganate stain, can be easily and rapidly visualized in a classroom setting.

KEYWORDS: First-Year Undergraduate/General, High School/Introductory Chemistry, Second-Year Undergraduate, Demonstrations, Organic Chemistry, Physical Chemistry, Alkenes, Aromatic Compounds, Oxidation/Reduction, UV-Vis Spectroscopy

FEATURE: Tested Demonstration



Conjugated double bonds represent one of the most important functionalities in organic chemistry and are a critical component in both optical materials and conducting polymers. The importance of conjugated π -bonds across chemistry and the physical sciences has been affirmed not only by the number of Nobel prizes in chemistry awarded for “fundamental” advances in this subject area (Baeyer, 1905, Willstätter 1915, Fischer 1930, Karrer 1937, Kuhn 1938, Diels and Alder 1950), but also the number of recent Nobel prizes, highlighting the relevance of conjugated and aromatic systems in emerging technologies, including the prizes for fullerenes (Kurl, Kroto, and Smalley in 1996),¹ conjugated polymers (Heeger, MacDiarmid, and Shirakawa in 2000),² fluorescent protein bioprobes (Shimomura, Chalfie, and Tsien in 2008),³ and graphene (Geim and Novoselov, Physics, in 2010).⁴

While the reactivity and physical properties of both aromatic rings and nonaromatic double bonds are standard subjects in the organic chemistry curriculum, oftentimes a simple informative classroom demonstration can effectively reinforce such fundamental concepts by providing a more experiential interaction with the subject material. For instance, brief mid-lecture demonstrations have been advocated as a needed break from note taking to enable students to refocus during the second half of class.⁵ The following brief classroom demonstration was designed to be easily carried out during a 5-min mid-lecture break. It probes both the UV fluorescence and chemical reactivity of a series of unsaturated hydrocarbons to visually enforce the spectroscopy of conjugated π -bonds as well as contrast alkene reactivity with aromatic stability.

DEMONSTRATION

Overview

This demonstration features a series of organic compounds containing multiple C=C double bonds. In advance, solutions of the unsaturated hydrocarbons should be prepared in dichloromethane, to be immobilized on silica-based thin-layer chromatography (TLC) plates. These loaded plates will be examined under UV light, and then oxidized with a potassium permanganate-based TLC stain, both requiring a benchtop camera interfaced with an overhead projector for classroom visualization. The compounds were selected to represent the major classes of unsaturated hydrocarbons, including polycyclic aromatic hydrocarbons,^{6,7} such as naphthalene, anthracene, and coronene; unconjugated nonaromatic terpenoids, such as squalene;⁸ as well as mixed aromatic–nonaromatic conjugated hydrocarbons, such as (1E,3E)-1,4-diphenylbuta-1,3-diene (Figure 1 and Table 1). This demonstration could be easily expanded to include other unsaturated hydrocarbons, though these were selected because of their availability and ease of visualization.

Required Chemicals

All of the unsaturated hydrocarbons are relatively common, can be purchased from Sigma-Aldrich, and were used without additional purification. The required chemicals for this demonstration are naphthalene, squalene, anthracene,

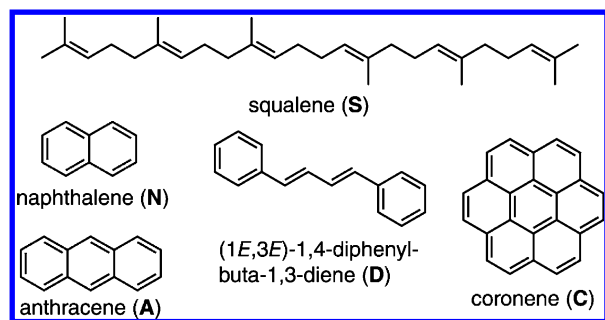


Figure 1. Structures, names, and abbreviations of the five unsaturated hydrocarbons analyzed in this study.

Table 1. Data for the Analytes

Compound (Abbreviation)	Molar Mass/ (g mol ⁻¹)	Number of Double Bonds	
		Total	Nonaromatic
Naphthalene (N)	128.17	5	0
Squalene (S)	410.72	6	6
Anthracene (A)	178.23	7	0
(1E,3E)-Diphenylbuta-1,3-diene (D)	206.28	8	2
Coronene (C)	300.35	12	0

(1E,3E)-1,4-diphenylbuta-1,3-diene, coronene, and dichloromethane (Figure 1). Dichloromethane was used to prepare 4 mM stock solutions (~5 mL) of each of the analytes.

Required Glassware and Materials

The following materials are needed to carry out the demonstration:

- A wide-mouth 250 mL screw-top jar to store the KMnO₄ stain (wide enough to enable dipping of the TLC plate)
- 5 scintillation vials (~10 mL) to hold stock solutions of each of the unsaturated hydrocarbons
- A 3 cm × 6 cm piece of aluminum backed TLC plate to immobilize the analytes
- A long-wave UV lamp (366 nm) for visualization of UV fluorescence
- A paper towel to remove excess permanganate stain from TLC plate
- Video camera—overhead projection system for enable classroom visualization

Preparation of the Permanganate TLC stain

In a clean 250 mL wide-mouthed, screw-top jar, 1.5 g of potassium permanganate, 10 g of potassium carbonate, and 0.125 g of potassium hydroxide were dissolved in 200 mL of water. The hydroxide and carbonate are added to yield a basic buffered solution. This solution should then be tightly sealed to avoid spillage or accidental contact with the skin and handled carefully with the appropriate safety apparel.

HAZARDS

The permanganate-based TLC stain is both strongly oxidizing and alkaline. Gloves, safety goggles, and laboratory jackets must be worn throughout the demonstration. Intense exposure to the UV irradiation can be damaging to the eyes or skin, and care must be taken to minimize the exposure to the audience and demonstrator. Contact with the hydrocarbon analytes and the dichloromethane solvent should be avoided as they may cause

irritation to the skin or eyes. In addition, proper ventilation and waste disposal must be considered during the classroom demonstration and subsequent cleanup. When disposing of excess chemicals, any dichloromethane solutions should be disposed with halogenated waste. Excess permanganate stain solution should be placed with aqueous waste, but should be neutralized first with a reducing agent (e.g., sodium bisulfite or oxalic acid) and mild acid, as it is both basic and oxidizing.

IN-CLASS DEMONSTRATION

Solutions of the 5 unsaturated hydrocarbons compounds can be prepared in advance in scintillation vials, as well as a TLC plate graduated and labeled with pencil (Figure 2A). Using a pipet as

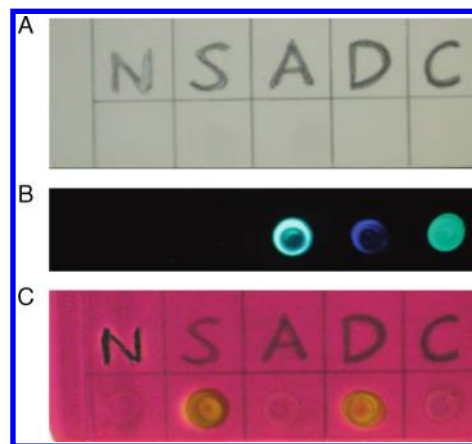


Figure 2. Visualization of TLC plate after immobilization of unsaturated hydrocarbons (A) by visible inspection, (B) under long-wave UV (366 nm) irradiation, and (C) after oxidation with potassium permanganate stain.

a “spotter”, the stock solutions were spotted onto the TLC plate; for each location, the samples were spotted 4 times, allowing the dichloromethane to dry in between spotting. The TLC plate can then be examined by the camera, to reveal no visible sign of the samples, apart from a faint yellow spot from the coronene sample. With the overhead lights dimmed, examination of the spots under long-wave UV irradiation shows fluorescence from the three compounds with the most double bonds: anthracene, (1E,3E)-1,4-diphenylbuta-1,3-diene, and coronene (Figure 2B). It should be noted that in order for a compound to exhibit fluorescence, it must contain a sufficiently extended set of conjugated double bonds to absorb long-wave UV light.⁹ In the case of squalene, although 6 double bonds are present, they are not conjugated, and therefore, it cannot fluoresce in the visible region. In the case of naphthalene, the five double bonds in the conjugated system are not sufficient to enable long-wave UV absorption. Therefore, only those compounds with a longer conjugated series of double bonds exhibit fluorescence. Finally, to explore susceptibility to oxidants, the TLC plate can be dipped into the potassium permanganate stain solution. The excess stain on the TLC plate should be allowed to pool at one of the edges of the plate and removed by dabbing the edge on a paper towel to minimize dripping or contamination from the potassium permanganate during handling. The effects of the permanganate stain are apparent, as the unreactive aromatic samples maintain the bright magenta color of the stain, whereas the oxidizable (nonaromatic) double bonds reduce the purplish Mn(VII)O₄⁻ to Mn(IV)O₂, resulting in a yellow–brownish discoloration for

both squalene and (1E,3E)-1,4-diphenylbuta-1,3-diene (Figure 2C). The hydrocarbon stock solutions and permanganate stain should exhibit sufficient stability to be reused within a month of their preparation if they are stored in sealed vials.

■ SUMMARY

By using TLC plates to immobilize a series of unsaturated hydrocarbons, their UV fluorescence and susceptibility to oxidation can be easily probed. Despite the repeated reinforcement of these concepts from both the textbook and lecture discussion, this fast and simple visual demonstration of these concepts can provide a much more powerful reinforcement of these critical concepts, as well as stress the utility of their UV properties and reactivity when characterizing unknowns.

■ AUTHOR INFORMATION

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Notes

Andrew Duncan (Department of Chemistry, Willamette College, Salem, OR 97301) tested this demonstration.

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- (9) The fluorescing dyes selected were chosen in part because they all exhibit sufficient quantum yields (efficient radiative relaxation) so as to give a visual response via UV fluorescence. It should be noted, however, that while all conjugated systems with greater than 6 conjugated double bonds should absorb UV light, some can relax via nonradiative pathways, and therefore do not exhibit fluorescence.