Tetrahedron Letters 53 (2012) 6433–6435

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

6-Aryldibenzo[*b*,*d*]pyrylium salts: synthesis and characterization of a reversible pH-driven optical and spectroscopic response

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ARTICLE INFO

Article history:
Received 27 August 2012
Revised 11 September 2012
Accepted 13 September 2012
Available online 21 September 2012

Keywords:
Dibenzo pyrylium
Polycyclic aromatic hydrocarbon
Heterocycle
Dye
Halochromism

ABSTRACT

This preliminary report describes the synthesis of three 6-aryldibenzo[*b*,*d*]pyrylium salts, a relatively unexplored structural unit. The optical and spectroscopic properties of the 6-aryldibenzo[*b*,*d*]pyrylium salts were examined as a function of pH. All three compounds displayed bright colors under acidic conditions and were colorless under basic conditions. The halochromism of the molecules was shown to be reversible.

Small positively charged polyaromatic hydrocarbons containing oxygen are well-known synthetic and naturally-occurring substances. Numerous preparations of compounds containing 9-aryldibenzo[*b*,*e*]pyrylium, or 9-arylxanthylium, aromatic heterocycle subunit have been reported (Fig. 1).[1] Important compounds that contain this subunit include various rhodamine and rosamine dyes, typically used as cell and tissue labels.[2–7] In these cases the xanthylium ion is highly stabilized by amino substituents at the C3 and C6 positions, causing the amino groups to carry the majority of the positive charge. Stabilized 9-arylxanthylium containing compounds have also been recently found to be organic photosensitizers in dye sensitized solar cell applications.[8,9] Additionally, less stabilized unsubstituted 9-arylxanthyliums have been synthesized and their reactivity and physical properties have been studied.[10–16] While 9-arylxanthylium salts are quite well known, compounds containing the isomeric 6-aryldibenzo[*b*,*d*]pyrylium aromatic heterocycle subunit are surprisingly rare (Fig. 1). To the author's knowledge, only three 6-aryldibenzo[*b*,*d*]pyrylium salts have been prepared to date.[17–19] No practical applications of these compounds were discussed in these early reports; however, further exploration of compounds containing this subunit could ultimately result in a new class of synthetic dyes much like their ubiquitous xanthylium analogs. Additionally, 6-aryldibenzo[*b*,*d*]pyrylium salts have the same carbon skeleton as nitrogen-containing 6-arylphenanthridinium dyes, such as ethidium bromide,[20] and are benzannulated analogs of flavylium-containing pigments,[21] such as anthocyanins.

We sought to expand the library of reported 6-aryldibenzo[*b*,*d*]pyrylium salts and explore their spectroscopic responses to changes in pH. Nucleophiles have been shown to attack flavylium cations at the C2 position[21] and are suspected to attack the C6 position[18] of 6-aryldibenzo[*b*,*d*]pyrylium cations. Given this, changes in pH have the potential to reversibly disrupt intramolecular charge transfer (ICT) in 6-aryldibenzo[*b*,*d*]pyrylium compounds containing a *para* electron donating unit. This could ultimately lead to applications in pH-sensitive, or halochromic, materials. To this end, perchlorate salts (**1**–**3**) have been synthesized and their spectroscopic character in both acidic and basic media has been explored.

Compound **1** is known but has been limited to characterization by melting point and elemental analysis.[18] Previous unsuccessful attempts were made to synthesize **2** by peroxidation and acid-promoted ring-expansion of 9-*p*-methoxyphenylfluorene: in this case the authors reported a brightly colored orange solution but could not afford a precipitate.[18] In this current study, all perchlorate salts (**1**–**3**) were prepared via Grignard addition of the appropriate arylmagnesium halide to 6*H*-benzo[*c*]chromen-6-one (Scheme 1). 6*H*-Benzo[*c*]chromen-6-one was synthesized using a Baeyer–Villiger oxidation of 9-fluorenone. Dehydration in a cold, stirring, ethereal solution of the intermediate hemiketal with a mixture of acetic anhydride and 70% perchloric acid was paramount for obtaining the desired products as solid precipitates. Numerous other methods were attempted that led to the products oiling out of solution.

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0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.09.054

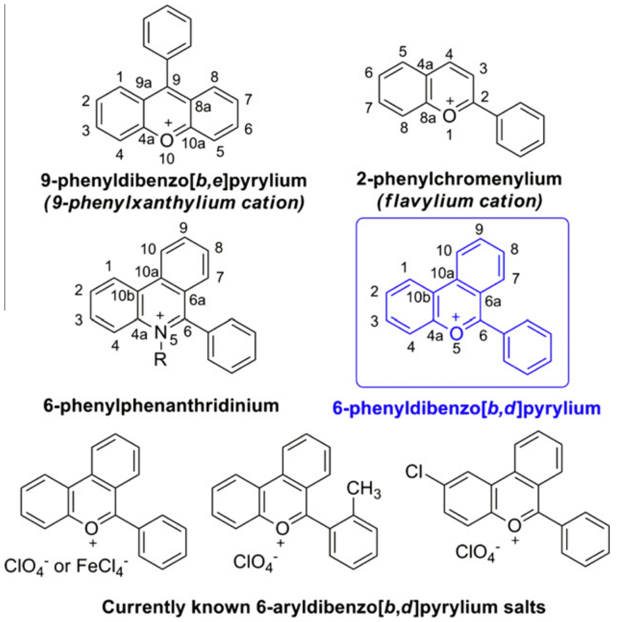


Figure 1. Structures of some positively charged heterocyclic aromatic compounds with commonly accepted numbering of atoms.

All three compounds were obtained as brightly colored solids (**1** = yellow, **2** = orange, **3** = metallic black/purple).

Naturally-occurring flavylium containing pigments, such as anthocyanins, are known to be sensitive to pH with an instantaneous halochromic response.[21] All three 6-aryldibenzo[*b*,*d*]pyrylium-containing compounds (**1**–**3**) are brightly colored in organic solution (Fig. 2) and upon addition of excess triethylamine (TEA), the solutions instantly become colorless. The colors of all three compounds return immediately upon addition of excess trifluoroacetic acid (TFA). Visual inspection indicated that the reversibility of the color changes was consistent through several cycles of acid/base additions.

Interestingly, compound **3** required more than ten times the volume of TEA, a weak base, to become completely colorless relative to compounds **1** and **2**. This is indicative of effective resonance stabilization of the pyrylium unit by the dimethylamino group in **3**. The extra stabilization of the dimethylamino group is also readily apparent by the nonlinear downfield trend in ^{13}C NMR chemical shifts at the C6 positions for all three compounds (see Supplementary data for full spectral details). Unsubstituted pyrylium **1** resonates at 184.9 ppm. Substitution with the *p*-methoxy unit decreases the C6 chemical shift to 182.4 ppm for **2**, a 2.5 ppm difference, whereas substitution with the *p*-dimethylamino unit decreases the C6 chemical shift to 178.5 ppm, a 6.4 ppm difference.

The pH-induced states of the 6-aryldibenzo[*b*,*d*]pyrylium salts were further analyzed by UV–vis spectroscopy (Fig. 3). Solutions of compounds **2** and **3** in acetonitrile both exhibit intramolecular charge transfer (ICT) bands in the visible region at 445 nm (ε = 20,478 M^{-1} cm^{-1}) and 548 nm (ε = 7251 M^{-1} cm^{-1}). The lower energy HOMO–LUMO band gap for **3** is once again more evident of the expected stabilization to the pyrylium unit by the dimethylamino group. Upon addition of excess triethylamine, none of the molecules absorb in the visible, thereby effectively disrupting conjugation between the electron donating groups and the pyrylium moiety.

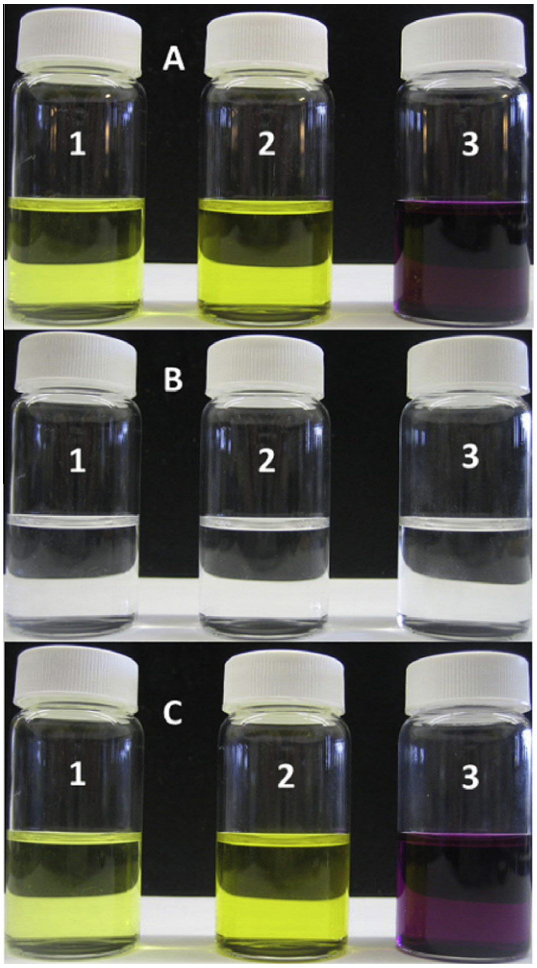
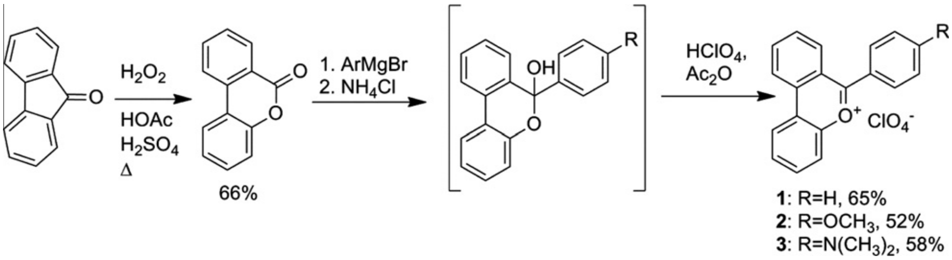


Figure 2. Photographs of **1**–**3**. Top (A): from left to right, compound **1** (0.56 mM), **2** (0.64 mM), and **3** (0.46 mM) in 10 mL of CH_3CN. Middle (B): solutions in (A) after addition of 10 μL (0.072 mmol) of TEA to **1**–**2** and 100 μL (0.720 mmol) of TEA to **3**. Bottom (C): solutions in (B) after addition of 200 μL (2.60 mmol) of TFA.

Numerous 9-arylxanthylium based compounds, such as rhodamine and rosamine, are very useful fluorescent dyes.[2–7] Compound **1**, containing a tetrachloroferrate counterion, was originally reported in 1909 and was initially indicated to be nonfluorescent.[17] We have also found that acetonitrile solutions of **1**–**3** are not *visibly*



Scheme 1. The synthesis of 6-aryldibenzo[*b*,*d*]pyrylium perchlorate salts.

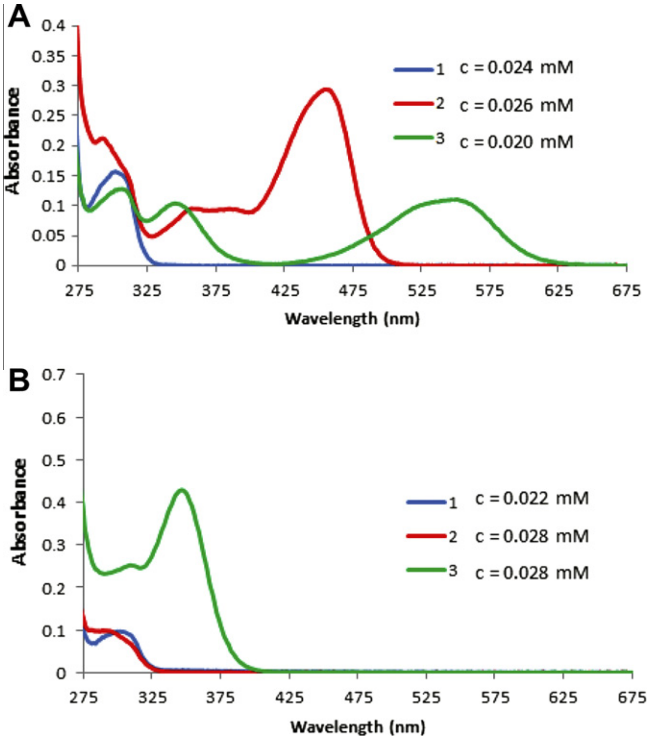


Figure 3. UV–vis spectra of **1**–**3**. Top (A): **1**–**3** in CH_3CN at the indicated concentrations. Bottom (B): **1**–**3** in CH_3CN at the indicated concentrations after addition of **1** drop of TEA.

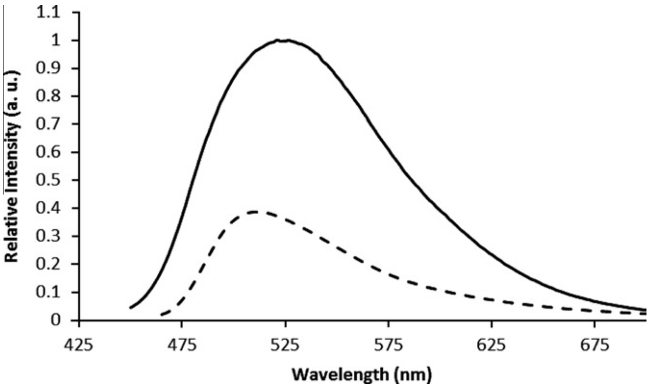


Figure 4. Emission spectra of **1** (solid line), 0.52 mM in CH_3CN and **2** (dashed line), 0.53 mM in CH_3CN. Compound **3** exhibited no detectable fluorescence. Compounds **1** and **2** did not fluoresce upon addition of TEA.

luminescent upon UV irradiation. However, **1** and **2** were indeed determined to be fluorescent upon closer inspection with spectrofluorometric analysis (Fig. 4). Compound **1** emits at 526 nm (excitation wavelength = 427 nm) and compound **2** emits with lower intensity at 515 nm (excitation wavelength 445 nm). Compounds **1** and **2** exhibit no detectable fluorescence upon addition of triethylamine. Compound **3** exhibited no detectable fluorescence in acetonitrile at any wavelength.

In summary, three colorful 6-aryldibenzo[*b*,*d*]pyrylium perchlorate salts (**1**–**3**) have been prepared in two steps from 9-fluorenone. Compounds **2** and **3** were previously unknown. All three compounds are brightly colored in solution and are optically and spectroscopically responsive to changes in pH. Compounds **1** and **2** were shown to be fluorescent, which could be completely diminished upon addition of TEA. These preliminary studies indicate that compounds containing the relatively unexplored 6-aryldibenzo[*b*,*d*]pyrylium subunit are simple to synthesize and could show promise in dye applications and as optical pH sensors. Future studies are planned to synthesize and examine other 6-aryldibenzo[*b*,*d*]pyrylium derivatives and to further explore their reactivity and dye properties.

Acknowledgments

Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund (ACS PRF 51259-UNI1) for support of this research. We also thank the National Science Foundation (CHE-0850701) and the Student Blugold Commitment Differential Tuition funds through the University of Wisconsin-Eau Claire Faculty/Student Research Collaboration Grants program for financial support.

Supplementary data

Supplementary data (details of spectroscopic studies, synthetic procedures, and characterization data for all new compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.09.054.

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