Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 127 (2014) 268–274

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Synthesis and chemosensitivity of a new iminium salt toward a cyanide anion

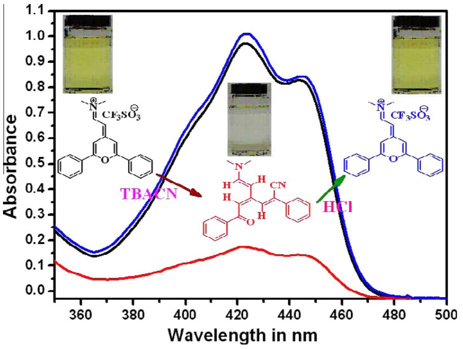
Boddu Ananda Rao, Jae-Young Lee, Young-A. Son *

Department of Advanced Organic Materials Science and Engineering, Chungnam National University, 220 Gung-dong, Yuseong-gu, Daejeon 305-764, South Korea

HIGHLIGHTS

- Synthesis of a new pyranylidene iminium (**Imi**) salt in high yields (92%).
- Pyranylidene iminium (**Imi**) salt can be used to determine CN$^-$ ion with high selectivity.
- **Imi** salt attracts the nucleophilic CN$^-$ ion to form the cyano-enone structure.
- Selective binding leads to ~171 nm [423–252 nm] hypsochromic (blue) shift.
- The binding mechanism and product identity were confirmed using FT-IR studies.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 October 2013
Accepted 12 February 2014
Available online 26 February 2014

Keywords:
Pyrylium trifluoromethanesulfonate
Pyranylideneiminium salt
Cyanide ion sensing
Chemosensor
Nucleophilic additions

ABSTRACT

A short, high-yielding route to pyranylidene Iminium (**Imi**) salts using a new pyrylium salt reaction between N,N-Dimethylformamide (DMF) and acetic anhydride is reported. The **Imi** salt-sensing behavior toward various anions has been investigated using UV–Visible spectroscopy. The **Imi** salt demonstrates high selectively for CN$^-$ when various other anions, such as CN$^-$, Cl$^-$, Br$^-$, I$^-$, SCN$^-$, ClO$_4^-$, NO$_3^-$, HSO$_4^-$, PF$_6^-$ and N$_3^-$, are present because it is highly reactive towards nucleophiles. The selective detection of CN$^-$ with the **Imi** unit gave rise to a significant hypochromic shift in the CH$_3$CN solution at λ_{max} = 444 nm and 423 nm and creation of new peak at 252 nm. These studies indicated that CN$^-$ had high affinity toward **Imi**, forming a 1:1 complex; this observation agrees with the current understanding of these materials.

Introduction

The first pyrylium and pyranylideneiminium (**Imi**) salts were synthesized nearly 100 years ago. During the first half of the present century, interest in these compounds was reasonable [1]. Among the six membered heterocycles containing one heteroatom, the pyrylium cation is the most strongly perturbed benzenoid system with a low aromaticity [2,3]; however, pyrylium salts are good synthons for numerous chemical reactions and a nodal point for many synthetic routes. They may function as intermediates for various synthetic applications [4]. Pyrylium rings are able to react with different nucleophiles according to the steric or electronic effects caused by the substituents; the nucleophile may also selectively add in either the α- or γ-position to create 2H- or 4H-pyrans, respectively, Unless the γ-position is unsubstituted or the nucleophile is small or unselective (e.g., hydrides, Grignard reagents), addition to the α-position is preferred because the α-position is more electron deficient than the γ-position. Both positions may undergo subsequent reactions to generate acyclic end products

---

* Corresponding author. Tel.: +82 42 821 6620; fax: +82 42 821 8870.
E-mail address: yason@cnu.ac.kr (Young-A. Son).

http://dx.doi.org/10.1016/j.saa.2014.02.052
1386-1425/

that may be converted into other ring systems [5]. One of the more important pyrylium ring transformation reactions is the generation of **Imi** salts. Pyrylium salts containing active methyl groups produce mono-iminium salts with DMF in acetic anhydride using the Vilsmeier complex. Donor–acceptor (D–A) **Imi** salt derivatives are interesting because they have interesting optical properties. Therefore, **Imi** salt derivatives are well-known laser dyes, and many of these derivatives are also useful red dopants for organic light-emitting diodes (OLED) [6]. In most cases, the pyranylidene moiety is incorporated into the π-spacer, generating either one-dimensional (1D) or two-dimensional (2D, also called V-shaped) [7] nonlinear optical (NLO) D–A and D–A–D type chromophores, respectively [8–10]. We have synthesized new 4-methyl 2,6-diphenyl pyrylium trifluoromethanesulfonate and **Imi** salts. These salts were described previously with different counter anions. The reported method used to synthesize **Imi** salts involved 4-methyl 2,6-diphenyl pyrylium perchlorate and DMF reacting within acetic anhydride [11,12].

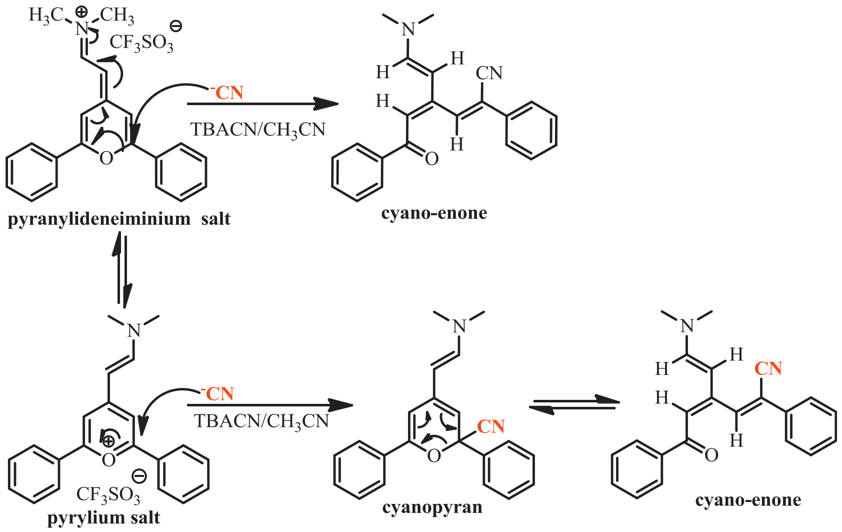
Anion sensors are important in biological, environmental, and industrial processes. Cyanide (CN^-) is the most toxic inorganic anion; it is acutely toxic to mammals when administered through any route, causing death in minutes [13]. CN^- strongly interacts with the cytochrome a_3 active sites and inhibits cellular respiration in mammalian cells [14,15]. Cyanide fishing [16] also pollutes waters in areas used for fishing for exotic fish, such as the coral reefs, and is a component of tabun, which is a chemical warfare agent [17]. Currently, various analytical methods have been developed to determine cyanide ion content, such as chromatographic [18], fluorometric [19], flow injection [20] and electrochemical [21] analyses. Many analytical techniques, such as potentiometry, chromatography and flow injection have been developed to detect cyanide [22,23]. Recently, nucleophilic addition of cyanide to pyrylium salt derivatives has also been adopted to sense CN^- [24]. This type of recognition exploits the nucleophilicity of the cyanide ion and enables the construction of a system that recognizes the characteristic features of CN^-, generating a specific response. C—C bond formation was observed with the pyrylium salt and its derivatives when used as colorimetric sensors for cyanide ions. The pyran's electrophilicity and CN^-'s nucleophilicity combine to form cyano-enone derivatives in CH_3CN solution [25,26]. Consequently, this reaction-based method might be developed to create a platform for discovering new **Imi** salts resembling sensors that may be potentially useful to detect CN^- in industrial, environmental, and biological capacities. Based on earlier reports, we propose the binding mechanism between **Imi** and CN^- ions, as displayed in Scheme 1.

Based on this hypothesis, we designed and synthesized a new small molecular sensor pyranylidene iminium (**Imi**) salt based on a pyrylium salt derivative and a suitable chromogenic organic group to develop a new chromogenic with enhanced sensing properties. We describe the synthesis and the binding properties of **Imi** salt chemosensor that display highly selective absorption changes with cyanide in the presence of various anions. We have explored a new one-pot synthesis to prepare the 4-methyl 2,6-diphenyl pyrylium trifluoromethanesulfonate salt using benzoyl chloride, anhydrous *t*-butyl alcohol and trifluoromethanesulfonic acid in high yields (>90%) for the primary step. Finally, reacting the pyrylium salt with DMF and acetic anhydride produces the **Imi** salt in high yields (>92%), as presented in Scheme 2. The sensor performance was not affected by other ions, demonstrating the high selectivity of this sensor toward cyanide. Therefore, in this paper we wish to report the design and synthesis of an **Imi** salt and its unique interaction with cyanide ion.

Materials and methods

Materials and apparatus

All solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless otherwise noted. AVANCE III 600 Magnet: Ascend™ series, 14.1 T, ^{1}H resonance frequency 600 MHz, ^{13}C resonance frequency 150 MHz, Top Spin 3.1 (software), Germany and JNM-AL400, 9.4 T, ^{1}H resonance frequency 400 MHz, ^{13}C resonance frequency 100 MHz, Alice 4.0 (software), Akishima, Japan spectrometers respectively, in CF_3COOD, DMSO-d_6 and $CDCl_3$ solvents were purchased from Sigma–Aldrich. The chemical shifts (δ values) were reported in ppm down field from an internal standard (Me_4Si) (^{1}H and ^{13}C NMR). The mass spectra were recorded with a JEOL MStation [JMS-700] mass spectrometer. FTIR spectra were recorded with a FTS-175C spectrometer (Bio-laboratories, Cambridge, USA). Melting points were recorded with a Bamstead electrothermal (UK) apparatus and are reported uncorrected. Elemental analyses were performed with a Carlo Elba Model 1106 analyzer. UV–Visible absorption spectra were recorded with an Agilent 8453 spectrophotometer. HOMO/LUMO (Highest Occupied Molecular Orbital/Lowest Unoccupied Molecular Orbital) calculations



Scheme 1. A plausible mechanism for the formation of the pyranylidene iminium salt (**Imi** salt) and its cyano-enone derivatives.