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Halochromism of pyridinium azomethine ylides stabilized by dicyanopyrazine group

Young-Sik Jung[a], Jae-Yun Jaung[b,*]

[a]*Medicinal Science Division, Korea Research Institute of Chemical Technology, P. O. Box 107, Yusong, Taejon 305-606, Republic of Korea*
[b]*Department of Polymer & Textile Engineering, Hanyang University, Haengdang-dong, Sungdong-gu, Seoul 133-791, Republic of Korea*

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Abstract

Reactions of 2-bromomethyl-3-phenyl-5,6-dicyanopyrazine with methyl substituted pyridine gave dicyanopyrazylmethylene pyridinium bromides. These salts were changed to their corresponding methylides by the addition of a base, which were restored by the addition of an acid. The pyridinium methylides exhibited intense visible absorption. This study was attempted to apply the pyridinium halides with a dicyanopyrazine group to a reversibly colored material to gain an external response. The 1,3-dipolar cycloaddition reaction of such pyridinium azomethine ylides containing a stabilized dicyanopyrazine group with dimethyl acetylenedicarboxylate (DMAD) afforded the indolizine derivatives.

Keywords: Azomethine ylides; Dicyanopyrazine; Dipolar cycloaddition; Halochromism; Indolizine; Fluorescence efficiency

1. Introduction

Pyrazine has two nitrogen atoms instead of the carbon atoms at 1 and 4 positions in a benzene ring, and is anticipated to have many functionalities and reactivities in comparison with their benzene analogues. 2,3-Dicyanopyrazines are generally known as very powerful electron acceptors and especially suitable for building blocks as a strong intramolecular charge transfer chromophoric system for the dye materials [1–3]. A typical characteristic of dicyanopyrazine based dye materials is their strong fluorescence which is currently of interest in the following fields: emitters for electroluminescence devices, solar energy collecting materials, energy-transfer materials and other fluorescent materials for various applications.

In continuing efforts to develop functional dyes based on dicyanopyrazine chromophores, our interest has focused on pyridinium azomethine ylides containing dicyanopyrazines and their 1,3-dipolar cycloaddition reaction with dipolarophiles, as the indolizine cycloadducts containing dicyanopyrazines are our target molecules that may potentially meet this end. Dyes and pigments generally possess satisfactory color, and good color fastness properties against light and heat, and additional properties such as a near infrared absorption, pleochroism and photoconductivity [4,5]. The majority of these properties are caused by intramolecular charge-transfer interactions involving π-electrons and intermolecular π–π interactions of the dye chromophores.

In this paper, indolizine derivatives were synthesized by the 1,3-dipolar cycloaddition reactions of pyridinium azomethine ylides containing a stabilized dicyanopyrazine group with dimethyl acetylenedicarboxylate (DMAD), which is one of the most reactive dipolarophiles. Their fluorescence properties and halochromism

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* Corresponding author. Tel.: +82 2 2290 0492; fax: +82 2297 5859.
E-mail address: jjy1004@hanyang.ac.kr (J.-Y. Jaung).

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were also studied to evaluate structure–property relationships.

2. Results and discussion

2.1. Reaction of pyridinium azomethine ylides stabilized dicyanopyrazine group with dimethyl acetylenedicarboxylate

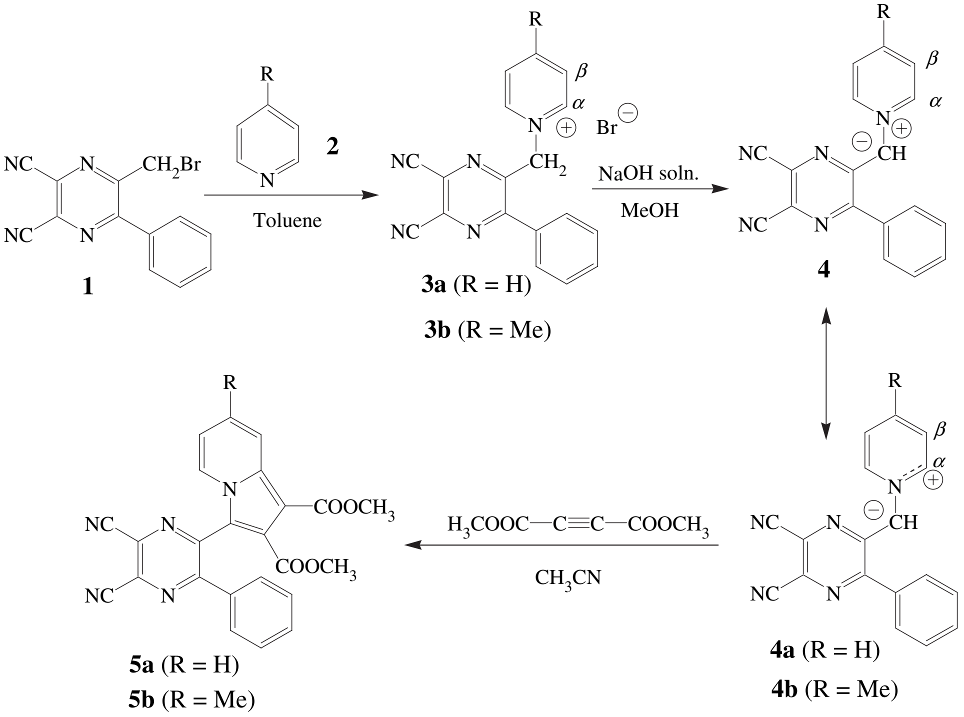
Several methods have been developed for functionalizing dicyanopyrazines. In a previous paper, the condensation reaction of 2,3-disubstituted-5,6-dicyanopyrazine with various arylaldehydes gave good yields of the corresponding fluorescent styryl dyes [5].

The treatment of 4-methyl pyridine (**2b**) with 1.0 equiv. of 2-bromomethyl-3-phenyl-5,6-dicyanopyrazine (**1**) at refluxing temperature in toluene afforded 1-[5-(2,3-dicyano-6-phenylpyrazinyl)-methylene]-4-methylpyridinium bromide (**3b**) in 75% yield (Scheme 1).

Although, pyridinium halides with an electron withdrawing group N-α-position are easy to undergo dehydrohalogenation by the addition of a base to give corresponding pyridinium methylides [6,7]. Azomethine ylides are generally unstable species, which must be prepared and used in situ, and are often isolated in the case of pyridinium azomethine ylides. The methylene protons of compound **3** are quite acidic due to their location between the dicyanopyrazine and pyridinium groups. Thus, the isolation of 4-methyl pyridinium-2,3-dicyano-6-phenyl-5-pyrazinylmethylide (**4**) was attempted. The treatment of **3** with aqueous sodium hydroxide in methanol provided a dark red colored ylide **4** as a solid. The ylide **4** dissolved in most polar organic solvents including acetonitrile and tetrahydrofuran (THF).

The proton NMR spectra showed the methylene proton of compound **3a** at around 6.60 ppm, while that of 1,1′-dibenzyl-4,4′-bipyridyl dibromide was observed at 5.95 ppm. Due to the strong electron withdrawing ability of the dicyanopyrazine moieties, the methylene proton is very acidic, and favorable to a deuterium exchange. The integral value for the methylene proton was decreased by more than 80% on the addition of D_2O to the DMSO-d_6 solution of compound **3** (Fig. 1). The signals of the pyridinium protons of **3b** appeared as doublets at 8.85 ppm and 8.09 ppm, and those of the pyridinium protons of **4b** appeared as doublets at 9.18 ppm and δ 7.71 ppm. The downfield shifts of the α-proton of **4** were attributed to the 1,3-dipole formation due to the positive charge delocalization. However, the signals of other pyridyl protons of **4** were observed as doublets at the upper field to those of **3**, which was caused by the electron donating ability of the ylide anion.

The assignment of the methylide was further supported by the formation of a 1,3-dipolar cycloadduct. The azomethine ylide, a useful 1,3-dipole, has been used to prepare five membered heterocycles containing one nitrogen atom, i.e. pyrroles, pyrrolines, and



Scheme 1.

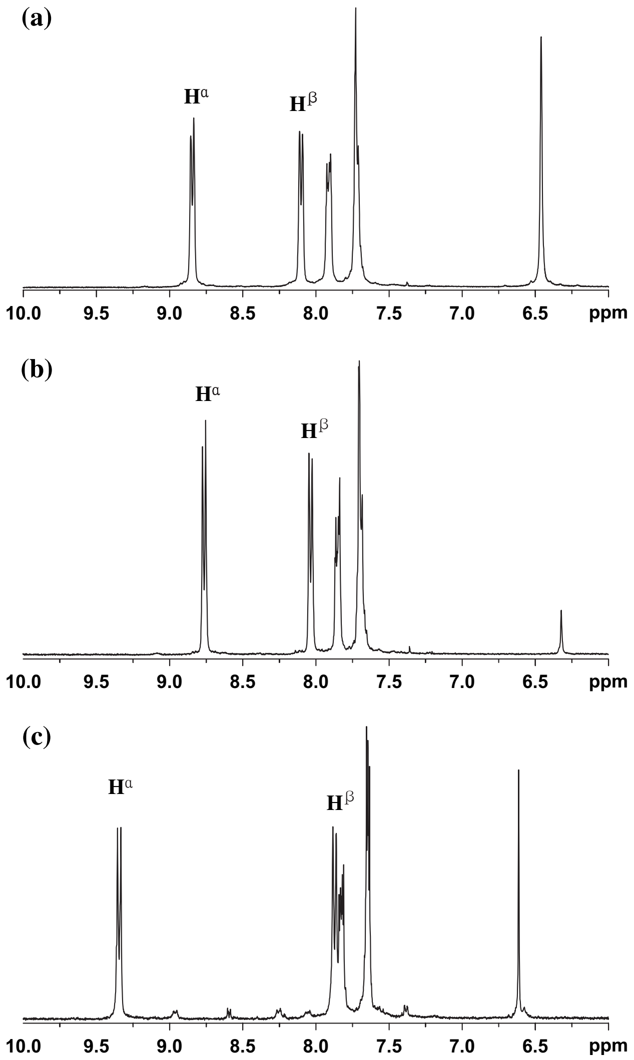


Fig. 1. ^{1}H NMR spectra of **3b** and **4b**; (a) **3b** in DMSO-d_6, (b) addition of D_2O to (a), (c) **4b** in DMSO-d_6.

pyrrolidines. The 1,3-dipolar cycloaddition reactions of **4** with DMAD, one of the most reactive dipolarophiles, in anhydrous acetonitrile without a base at room temperature provided the indolizines containing 5,6-dicyanopyrazine (**5**) in 23% yields in 2 conversion steps from **3** after column chromatography and recrystallization from methanol. The results are summarized in Table 1 and Scheme 1.

2.2. Absorption and emission spectra

The reaction of dicyanopyrazinylmethylene pyridinium bromide with a base resulted in an intensely colored methylide, which was reversibly restored with an acid. This reversible reaction can be repeated by alternately applying anode and cathode potentials in the electrochemical reaction. The absorption spectra of compounds **3** and **4** in acetonitrile were measured at the cathode after electrocoloration in the presence of tetrabutylammonium perchlorate as an electrolyte. By changing the polarity of the electrode, colored solutions turned colorless.

Table 1
Reaction results of **3**–**5**

Compounds	**3a**	**3b**	**4a**	**4b**	**5a**	**5b**
R	H	Me	H	Me	H	Me
m.p. (°C)	210[a]	218[a]	175–177	178–179	192–193	176–177
Yield (%)	73	75	80	87	29	25

[a] Decomposition.

In the earlier stage of this work, it was assumed that the colored species ($\lambda_{max} = 502$ nm) formed on applying a cathodic voltage to **3a** were the corresponding radical cation of **3a** such as that of 1,1′-dibenzyl-4,4′-bipyridyl dibromide. However, the absorption spectra of compounds **3a** and **3b** at the cathode showed the same patterns as those of **4a** ($\lambda_{max} = 502$ nm, $\varepsilon = 46{,}228$) and **4b** ($\lambda_{max} = 500$ nm, $\varepsilon = 44{,}449$) in DMSO solution.

An aqueous solution showed a drastic pH change in the cathodic and anodic sides. Applying a cathodic voltage turned the surroundings basic, but conversely, the anode compartment became acidic. Applying a potential to these compounds may be more preferable to an acid–base reaction, resulting in a reversible color change (halochromism), unlike to that of 1,1′-dibenzyl-4,4′-bipyridyl dibromide which produces cation radicals under the same condition [8–10].

These colored pyridinium methylides were unusually stable even in acetonitrile solution, suggesting the delocalization of the ylide carbanion over the whole molecule. The deprotonation of pyridinium bromide by a base may make both the pyrazine and pyridyl rings considerably coplanar, enhancing the electron conjugation between the two rings (Fig. 2).

As shown in Table 2 for dye **5**, the absorption and fluorescence maxima were observed at 435–452 nm and 508–589 nm, respectively. The resulting bathochromic

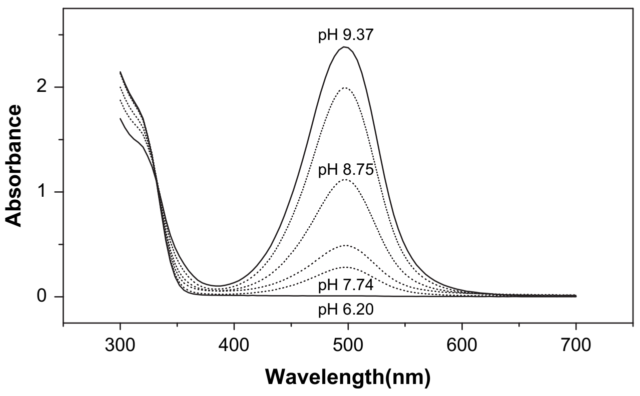


Fig. 2. Absorbance change of **3** in buffer solution.

Table 2
Visible and fluorescence spectra of **5**

Compounds	Ethanol		Acetonitrile		Ethyl acetate		THF	
	λ_{max} (nm)	F_{max} (nm)[a]	λ_{max} (nm)	F_{max} (nm)[a]	λ_{max} (nm)	F_{max} (nm)[a]	λ_{max} (nm)	F_{max} (nm)[a]
5a	438	508	440	540	435	583	440	550
5b	447	511	452	532	449	589	450	575

[a] Fluorescence maximum excited at λ_{max} value.

shift of 9 nm compared to dye **5a**, in ethanol, was attributed to the larger basicity of the indolizine moiety.

However, the fluorescence maximum of dye **5** showed a hypsochromic shift with an increase in the solvent polarity and the effects of solvent polarity on the fluorescence spectra of **5b** are shown in Fig. 3. In the non-polar solvents, dye **5** exhibited reasonably higher fluorescence efficiency than that in protic polar solvents under the same concentration. It is generally known that the formation of an exciplex in the solid state or a concentrated solution causes fluorescence quenching [11]. Therefore, the fluorescence properties of indolizines **5** may be influenced greatly by the molecular aggregation.

3. Experimental

3.1. General

All reactions were carried out under N_2 atmosphere unless otherwise noted. 2-Bromomethyl-3-phenyl-5,6-dicyanopyrazine (**1**) [5] was prepared by the known methods. MeCN was distilled from CaH_2 prior to use. Organic extracts or filtrates were washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Flash chromatography was performed with Merck-EM Type 60 (230–400 mesh) silica gel (flash). ^1H NMR spectra were measured by Varian Gemini 200 MHz spectrometers. Mass spectrometric data determined by use of the electron impact (EIMS) method are reported as *m/z* (relative intensity). Elemental analyses were performed with CE Instruments-EA 1110 Automatic Elemental Analyzer. Melting points were uncorrected.

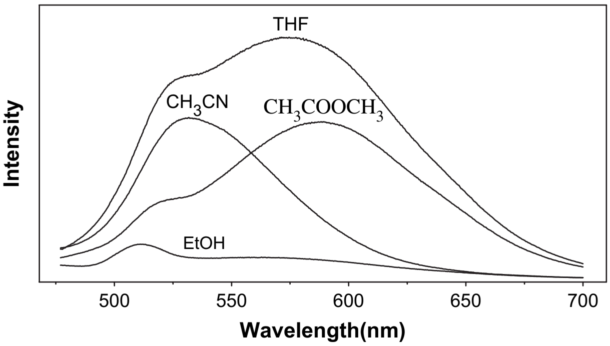


Fig. 3. The effects of solvent polarity on the fluorescence spectra of **5b** in the same concentration state.

3.2. Typical procedure for pyridinium bromides 3

A solution of 2-bromomethyl-3-phenyl-5,6-dicyanopyrazine (**1**) (2 mmol) and pyridine (**2a**) (1 mmol) in toluene (15 ml) was refluxed for 4 h under nitrogen atmosphere and then cooled to room temperature. The resulted precipitate was filtered, washed with benzene to give **3a** as white solids.

3.2.1. 1-[5-(2,3-Dicyano-6-phenylpyrazinyl) methylene]-4-pyridinium bromide (3a)

^1H NMR (DMSO-d_6) δ 6.60 (2H, s, CH_2), 7.70 (3H, m, phenyl protons), 7.91 (2H, m, phenyl protons), 8.29 (2H, t, *J* 7.8 Hz, pyridyl protons), 8.76 (1H, t, *J* 7.8 Hz, pyridyl proton), 9.09 (2H, d, *J* 7.8 Hz, pyridyl protons).

Anal. Calcd. for $C_{18}H_{12}BrN_5$: C, 57.16; H, 3.20; N, 18.52. Found: C, 57.08; H, 3.33; N, 18.40.

3.2.2. 1-[5-(2,3-Dicyano-6-phenylpyrazinyl) methylene]-4-methylpyridinium bromide (3b)

^1H NMR (DMSO-d_6) δ 2.68 (3H, s, CH_3), 6.48 (2H, s, CH_2), 7.68 (3H, m, phenyl protons), 7.92 (2H, m, phenyl protons), 8.09 (2H, d, *J* 6.4 Hz, pyridyl protons), 8.85 (2H, d, *J* 6.4 Hz, pyridyl protons).

Anal. Calcd. for $C_{19}H_{14}BrN_5$: C, 58.18; H, 3.60; N, 17.85. Found: C, 57.91; H, 3.63; N, 17.72.

3.3. Typical procedure for azomethine ylides 4

To a stirred solution of **3a** (2 mmol) in methanol (15 ml) under dry nitrogen at room temperature was added 1 ml of 5 N sodium hydroxide solution. After 0.5 h of stirring, the resulted precipitate was filtered, washed with ethanol to give ylide **4a** as dark red solids.

3.3.1. 1-[Pyridinium-(2,3-dicyano-6-phenylpyrazinyl)] methylide (4a)

^1H NMR (DMSO-d_6) δ 6.51 (1H, s, CH), 7.48 (3H, m, phenyl protons), 7.67 (2H, m, phenyl protons), 7.90 (3H, m, pyridyl protons), 9.34 (2H, d, *J* 5.7 Hz, pyridyl protons); MS *m/z* (relative intensity) 296.90 (M^+, 0.13), 130.00 (1.56), 79.00 (100).

Anal. Calcd. for $C_{18}H_{11}N_5$: C, 72.72; H, 3.73; N, 23.56. Found: C, 72.48; H, 3.80; N, 23.27.

*3.3.2. 1-[4-Methylpyridinium-(2,3-dicyano-6-phenyl-pyrazinyl)]methylide (**4b**)*

^{1}H NMR (DMSO-d_6) δ 2.43 (3H, s, CH_3), 6.44 (1H, s, CH), 7.44 (3H, m, phenyl protons), 7.63 (2H, m, phenyl protons), 7.71 (2H, d, J 6.7 Hz, pyridyl protons), 9.18 (2H, d, J 6.7 Hz, bipyridyl protons); MS m/z (relative intensity) 308.90 (M^+-2, 0.35), 219.00 (3.22), 93.00 (100).

Anal. Calcd. for $C_{19}H_{13}N_5$: C, 73.30; H, 4.21; N, 22.49. Found: C, 73.02; H, 4.28; N, 22.23.

*3.4. Typical procedure for 1,3-dipolar cycloaddition reactions of the ylide **4** with DMAD*

A mixture of **4a** (0.800 g, 2.70 mmol) and DMAD (1.14 g, 8.02 mmol) in anhydrous acetonitrile (30 ml) was stirred at room temperature for 12 h. Concentration of the mixture under reduced pressure afforded an oily product, which was purified by flash chromatography (silica gel, hexane–ethyl acetate, 2:1) to provide **5a** (0.378 g, 31%) as a solid. Further purification of the solid by recrystallization from methanol gave **5a** as a yellow crystal (0.341 g, 29%).

*3.4.1. 1,2-Dicarbomethoxy-3-(2,3-dicyano-6-phenyl-pyrazinyl)-indolizine (**5a**)*

^{1}H NMR ($CDCl_3$) δ 3.62 (3H, s, CO_2CH_3), 3.87 (3H, s, CO_2CH_3), 6.82 (1H, ddd, J 7.2, 6.8, 1.4 Hz, ArH), 7.23–7.51 (6H, m, ArH), 8.11 (1H, dt, J 7.2, 1.0 Hz, ArH), 8.28 (1H, dt, J 9.0, 1.2 Hz, ArH); MS m/z (relative intensity) 437 (M^+, 890), 405(29), 374(39), 346(40), 319(100).

Anal. Calcd. for $C_{24}H_{15}N_5O_4$: C, 65.90; H, 3.46; N, 16.01. Found: C, 65.88; H, 3.57; N, 15.97.

*3.4.2. 1,2-Dicarbomethoxy-3-(2,3-dicyano-6-phenyl-pyrazinyl)-7-methylindol-izine (**5b**)*

^{1}H NMR ($CDCl_3$) δ 2.42 (3H, s, CH_3), 3.61 (3H, s, CO_2CH_3), 3.85 (3H, s, CO_2CH_3), 6.66 (1H, dd, J 7.0, 2.0 Hz, ArH), 7.26–7.53 (5H, m, ArH), 8.04 (1H, d, J 7.0 Hz, ArH), 8.06 (1H, s, ArH); MS m/z (relative intensity) 451 (M^+, 90), 420(29), 388(31), 360(40), 333(100).

Anal. Calcd. for $C_{25}H_{17}N_5O_4$: C, 66.52; H, 3.76; N, 15.51. Found: C, 66.38; H, 3.81; N, 15.43.

Acknowledgements

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