

Dicyanopyrazine 계열의 기능성 색소 합성과 New Chromism

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Synthesis and keto-enol isomerism of Dicyanopyrazine-related Functional Dyes

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INTRODUCTION

Diaminomaleonitrile (DAMN) as a tetramer of hydrogen cyanide has considerable synthetic potential that has not been fully utilized because hydrogen cyanide is toxic and explosive, and thus many researchers are reluctant to use it. We believe that DAMN will eventually become a major building block for heterocyclic syntheses and are engaged in research to exploit hydrogen cyanide chemistry [1].

We have studied the syntheses of functional dye materials based on dicyanopyrazine chromophores, and correlated their physical properties with their structure [2,3]. New dicyanopyrazine-related heterocycles such as quinoxalines, pyrazinofuranes and pyrazinopyrroles were synthesized from DAMN. The Wittig reaction of 2,3-bis(bromomethyl)-5,6-dicyanopyrazine with 1,2-dicarbonyl compounds and the reaction of 2,3-dichloro-5,6-dicyanopyrazine with enamines were useful methodologies to extend the π -conjugation systems to give new heterocycles [4].

On the other hand, 2,3-dicyanopyrazines act as very powerful electron acceptors and are especially suitable building blocks for strong intramolecular charge-transfer chromophoric systems. The ensuing dyes have an ability to undergo strong intermolecular π - π interactions suitable for molecular stacking. One of the typical characteristics of dicyanopyrazine-based dye materials is their strong fluorescence which is currently of interest in the following application fields; emitters for electroluminescence devices, copy preventing inks, solar energy collecting materials, energy-transfer materials and other fluorescent materials for various applications.

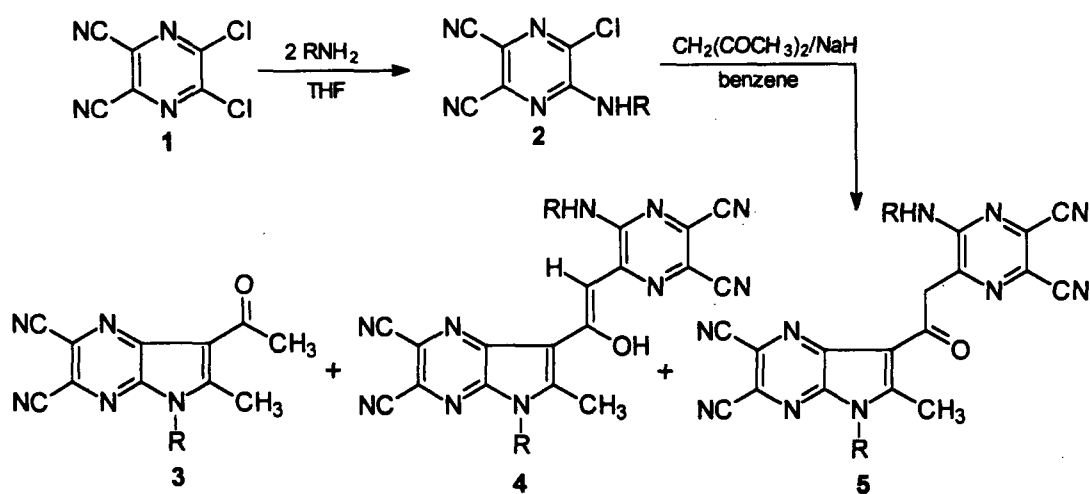
RESULTS AND DISCUSSION

Reaction of 2-alkyl or arylamino-3-chloro-5,6-dicyanopyrazine with pentane-2,4-dione We have developed several methods for functionalizing 2,3-dichloro-5,6-dicyanopyrazines. In a previous paper [7], nucleophilic substitution of 2,3-dichloro-5,6-dicyanopyrazine (1) with various nucleophiles such as amines, enamines and thiocarbonyl

compounds, gave the corresponding 2- and 2,3-disubstituted pyrazines in good yield. Treatment of **1** with two equivalent of amines in THF at low temperature afforded 2-amino products **2** in good yields (72 – 84%).

The reaction of **2** with 2,4-pentanedione in the presence of sodium hydride in dry benzene gave 2,3-dicyano-5-ethyl-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine **3**, 1-ethyl-2-methyl-5,6-dicyano-3{2-[5-ethylamino-2,3-dicyanopyrazin-6-yl]-1-hydroxyethenyl}-pyrrolo[2,3-*b*]pyrazine **4** and 1-ethyl-2-methyl-5,6-dicyano-3{2-[5-ethylamino-2,3-dicyanopyrazin-6-yl]-1-oxoethyl}-pyrrolo[2,3-*b*]pyrazine **5** in 47%, 14% and 3% yield, respectively. But similar reaction of 2-amino-3-chloro-5,6-dicyanopyrazine **2a** gave only 2,3-dicyano-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine **3a** because of low basicity of the amino group of **3a**. The results are summarized in Scheme 1.

The reaction of 2,3-dicyano-5-ethyl-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine **3b** with one equimolar proportion of **2d** in toluene under dry nitrogen in the presence of sodium hydride afforded the mixture of 1-ethyl-2-methyl-5,6-dicyano-3{2-[5-(4-*n*-pentylphenylamino)-2,3-dicyanopyrazin-6-yl]-1-oxoethyl}-pyrrolo[2,3-*b*]pyrazine **5e** and its enol derivative **4e** in 32% and 7% yield, respectively (Scheme 2). This result indicates that **3** is the precursor to **4** and **5**.



R = -H (a), -Et (b), -benzyl (c), 4-*n*-pentylphenyl (d)

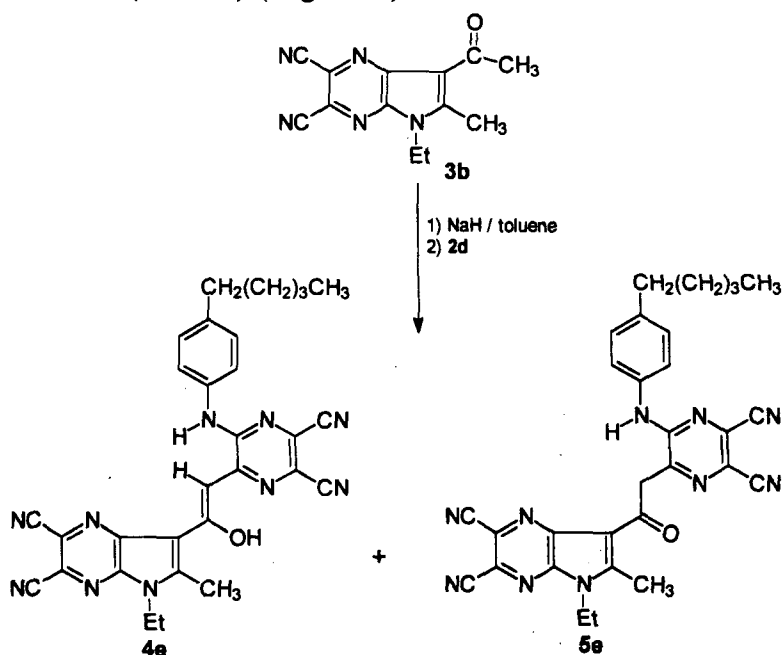
Scheme 1

Visible and Fluorescence Properties Compound **3** is small in molecular size and showed a blue fluorescence in solution as well as in the solid state. The absorption and fluorescence maxima of **3** were observed at 320~330nm and 480~490nm, respectively. The results are summarized in Table 2. The Stokes shift (ss) indicates the difference between F_{max} and λ_{max} and corresponds to energy loss in the first excited singlet state. Compounds **3** showed quite large ss values.

Compound **5** absorbed at 330~342nm and emitted at 460~470nm. The π -

conjugation of compound **5** is interrupted at the central methylene bond and its λ_{max} and ss values are comparable to those of **3**. The fully conjugated dyes **4** absorbed at around 530nm and showed a strong red fluorescence with a small ss values of 50~60nm. Their absorbance increased depending on the enlargement of π -conjugation.

Compounds **5** have the active methylene group and the keto form **A** and the enol form **B** may be possible to exist. The keto-enol isomerism of compounds **5** was observed in solution, and the isomerism was greatly influenced by the basicity of the solvent. The colour of dye **5d** in solution changed dramatically from colorless in chloroform to red in dimethylsulfoxide(DMSO) (Figure 1).



Scheme 2

TABLE 1
Visible and Fluorescence Spectra of **4** and **5**

Compound	λ_{max} (nm) ^a	log ϵ	F_{max} (nm) ^b	SS^c
4b	538	4.38	588	50
4c	532	4.41	590	58
4d	533	4.41	592	58
4e	533	4.42	590	57
5b	334	4.32	473	139
5c	335	4.32	471	136
5d	335	4.34	469	134
5e	336	4.33	469	133

^a In CHCl_3 . ^b Fluorescence maximum excited at λ_{max} value.
^c Stokes shift.

The keto form **A** was predominant in nonpolar solvents, while the enol form **B** was predominant in polar solvents such as DMSO. The absorbance of **5d** at around 590nm in DMSO decreased with increasing the concentration of acetic acid. The isosbestic points were observed at around 320 and 395nm, and two isomers will be included in DMSO. Similar spectra changes were also observed when triethylamine was added to the acetonitrile solution of dye **5**.

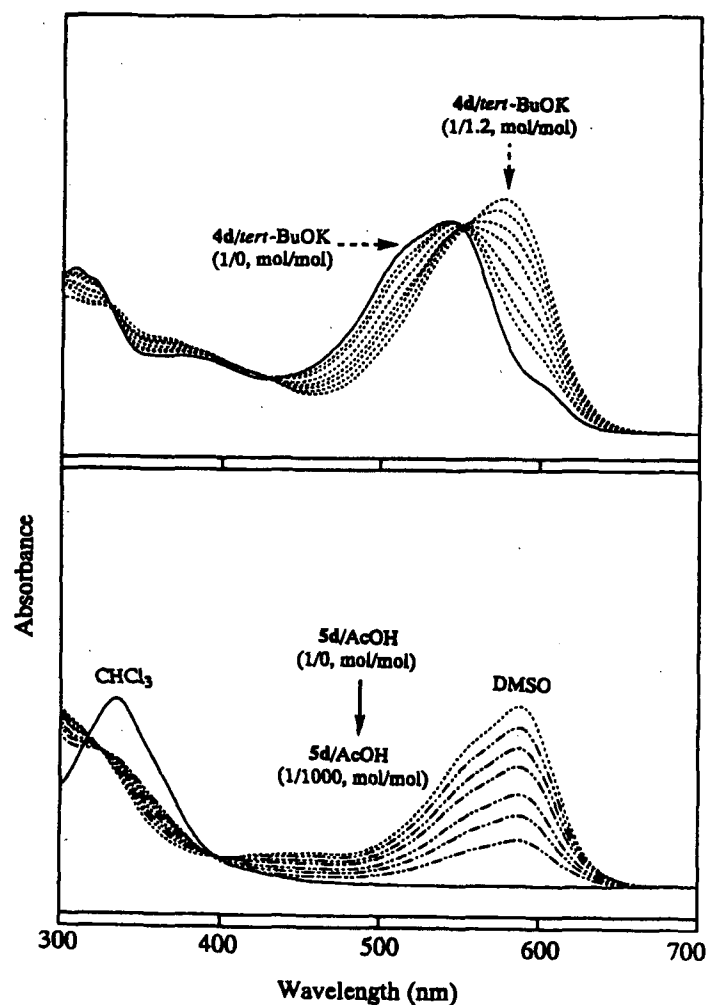


Figure 1

- The effects of acid and base on the absorption spectra of **4d** and **5d** in DMSO.
- (a). Addition of *tert*-BuOK (mol/mol) from 0 (solid line) to 1.2 (dotted line) for **4d**.
- (b). Addition of AcOH (mol/mol) from 0 to 1000 for **5d**. Solid line indicates the absorption spectra of **5d** in chloroform.

On the other hand, addition of potassium *tert*-butoxide to a DMSO solution of dye **4d** produced a bathochromic shift of the λ_{max} from 532 to 584nm. This absorption spectra is similar to that of **5d** in DMSO. From these observations, keto-enol isomerism of dye **5** caused deprotonation resulting from the strong electrostatic interactions occurring between the active methylene group and the basic solvent.

References

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