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Synthesis and keto–enol isomerism of 1-alkyl-2-methyl-5,6-dicyano-3-[2-(5-alkylamino-2,3-dicyanopyrazin-6-yl)-1-hydroxyethenyl]-pyrrolo[2,3-*b*]pyrazine

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Abstract

Reaction of 2-alkylamino-3-chloro-5,6-dicyanopyrazine **2** with 2,4-pentanedione in the presence of sodium hydride in benzene gave 2-methyl-3-acetyl-5,6-dicyanopyrrolo[2,3-*b*]pyrazine, which was further reacted with **2** to give the keto–enol mixtures of 3-[1-hydroxy-2-(3-alkylamino-5,6-dicyanopyrazine)-ethen-2-yl]-5,6-dicyanopyrrolo[2,3-*b*]pyrazine **4**. The keto-form of **4** is colorless in chloroform but red in dimethylsulfoxide (DMSO) as an enol-form. Their absorption spectra and electronic properties were correlated with their chemical structures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dicyanopyrazine; Keto–enol solvatochromism; Fluorescence; Absorption spectra; Isomerism; DAMN

1. 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

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following application fields; emitters for electroluminescence devices, copy preventing inks, solar energy collecting materials, energy-transfer materials and other fluorescent materials for various applications.

In general, one of the most elegant methods for carbon–carbon bond formation is the enamine synthesis developed by Curphey and coworkers [5]. The mild conditions under which enamines can be prepared, reacted with electrophiles, and the products hydrolyzed to α-substituted aldehydes and ketones have led to extensive utilization of enamines for synthesis of polyfunctional molecules. 2,3-Dichloro-5,6-dicyanopyrazine react with enamines to give the aminovinylpyrazines ultimately [6], but further ring closure-reaction of the terminal amino group with the second chlorine of 2,3-dichloro-5,6-dicyanopyrazine gives the corresponding heterocyclic compounds.

In this paper, the reaction of 2-alkylamino-3-chloro-5,6-dicyanopyrazine **2** with pentane-2,4-dione in the presence of sodium hydride was studied. The product of 2-methyl-3-acetyl-5,6-dicyanopyrrolo[2,3-*b*]pyrazine was further reacted with **2** to give the keto–enol mixtures of 3-[1-hydroxy-2-(3-alkylamino-5,6-dicyanopyrazine)-ethen-2-yl]-5,6-dicyanopyrrolo[2,3-*b*]pyrazine. The molecular dynamics of the reaction were deduced from their proton NMR spectra.

2. Results and discussion

2.1. 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 a 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 Table 1 and 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**.

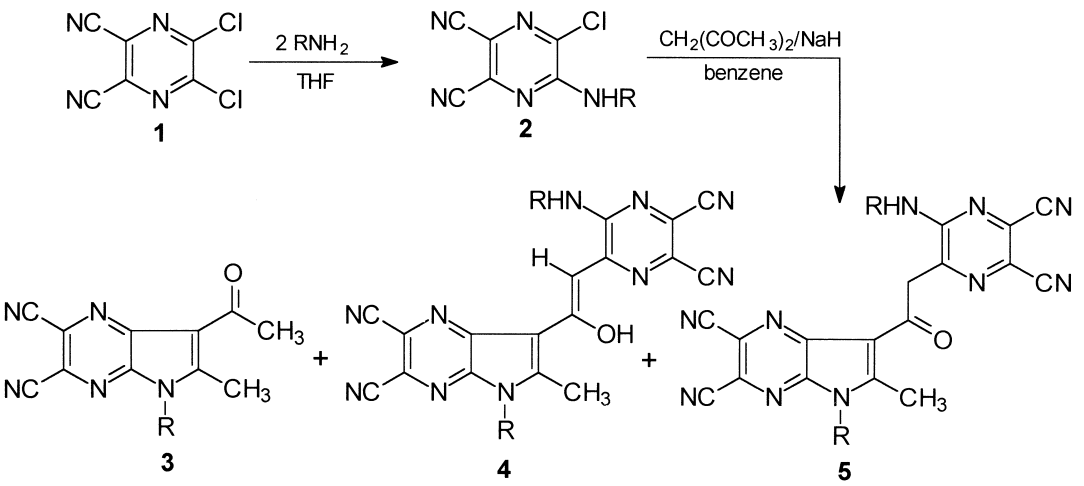
2.2. Visible and fluorescence properties

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 320–330 nm and 480–490 nm, 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.

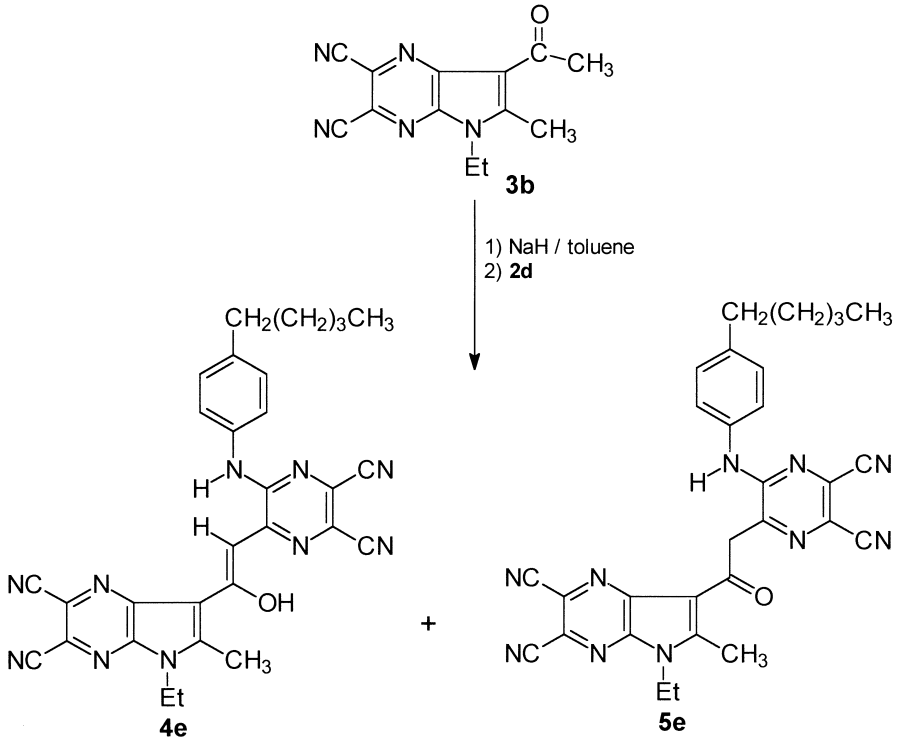
The visible and fluorescence spectra of dyes **4** and **5** are summarized in Table 3. Compound **5** absorbed at 330–342 nm and emitted at 460–470 nm. The π-conjugation of compound **5** is interrupted at

Table 1
Reaction of **2** with 2,4-pentadione

Run	R	Isolated yield (%)		
		3	**4**	**5**
1	-H	76	–	–
2	-Et	47	14	3
3	-Benzyl	50	12	Trace
4	4-Ph$(CH_2)_4CH_3$	44	16	3



Scheme 1. R = -H (a), -Et (b), -benzyl (c), 4-*n*-pentylphenyl (d).



Scheme 2.

Table 2
Visible and fluorescence spectra of **3**

Compounds	λ_{max} (nm)[a]	F_{max} (nm)[b]	SS[c]
3a	323	490	167
3b	326	480	154
3c	328	474	146
3d	326	477	151

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

Table 3
Visible and fluorescence spectra of **4** and **5**

Compound	λ_{max} (nm)[a]	$\log \epsilon$	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 central methylene bond and its λ_{max} and SS values are comparable to those of **3**. The fully conjugated dyes **4** absorbed at around 530 nm and showed a strong red fluorescence with a small ss values of 50–60 nm. 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 possibly 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) (Fig. 1). 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 590 nm in DMSO decreased with increasing the concentration of acetic acid. The isosbestic points were observed at around 320 and 395 nm, 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**.

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 584 nm.

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.

The proton NMR spectra show that the carbomethylene proton of dyes **5** was observed at around 4.88 ppm while acetyl proton of **3** was observed at around 2.93 ppm. The signal of ethenyl proton of **4b**, **4c** and **4d** appeared at 6.76, 6.85 and 6.65 ppm, respectively.

Fig. 2 shows the changes in ^{1}H-NMR spectra of **5d** by addition of potassium *tert*-butoxide to the deuteriochloroform (b) and the d_6-DMSO solution (c). The proton NMR spectra in $CDCl_3$ containing potassium *tert*-butoxide showed that the new proton signal appeared at 4.72 ppm assigned to the enolate proton H^b in Scheme 3. Due to the strong electron withdrawing ability of the 2,3-dicyanopyrazine moiety, the methylene proton of **5** is acidic and deprotonation easily occurred. As a result, the pyrazine and pyrrolopyrazine rings become considerably planar, and enhance electron conjugation between the two rings which produces the red colour of **4**. Consequently, the upper field shift of the H^b signal was attributed to the electron donating ability of the enolate resulting from deprotonation of the hydroxy group. The hydroxy proton ($\delta = 10.67$ ppm) of **4** was disappeared by addition of D_2O to the DMSO-d_6 solution.

Steric hindrance was observed at the *N*-benzyl group of **4c**; the methylene protons were observed at 5.34 (1H) and 5.67 (1H) ppm with $J = 16.8$ Hz, but the methylene protons of benzylamino group was observed at 4.57 (2H) ppm as doublet with $J = 16.8$ Hz.

3. Experimental

The identification of the compounds were carried out using the following equipment; melting

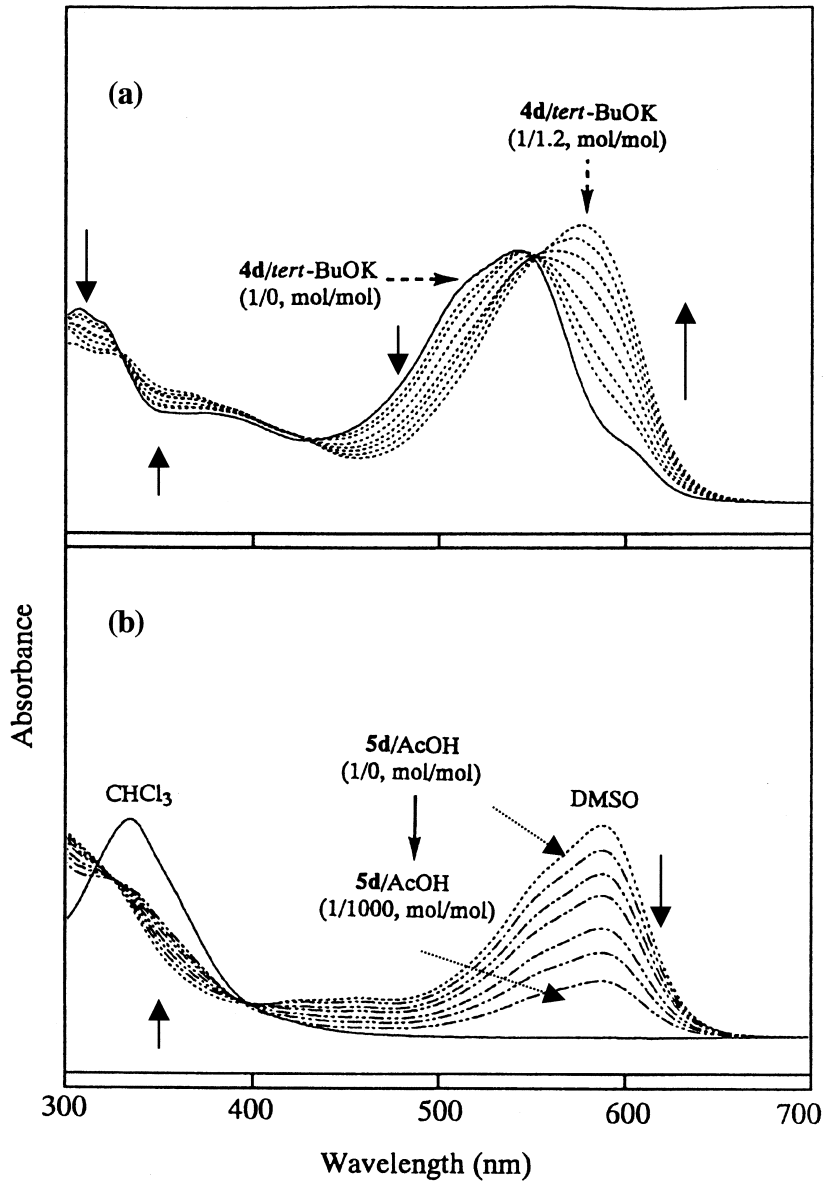


Fig. 1. The effects of acid and base on the absorption spectra of **4d** and **5d** in DMSO. (a) Addition of *tert*-BuOK (mol/mol) from 0 (solid line) to 1.2 (dotted line) for **4d**. (b) Addition of AcOH (mol/mol) from 0 to 1000 for **5d**. The solid line indicates the absorption spectra of **5d** in chloroform.

points were determined on a Yanagimoto micro melting point aparatus without correction. The PMR spectra were obtained using a FT-NMR QE 300 MHz GEC spectrometer. The MS spectra were recorded on a M-80 B Hitachi and Shimadzu GCM S-QP 5000 mass spectrometer. The visible and fluorescence spectra were measured on a U-3410 Hitachi spectrophotometer and a Shimadzu RF-5000 fluorescence spectrophotometer respectively. Microanalysis was conducted with a Yanaco CHN

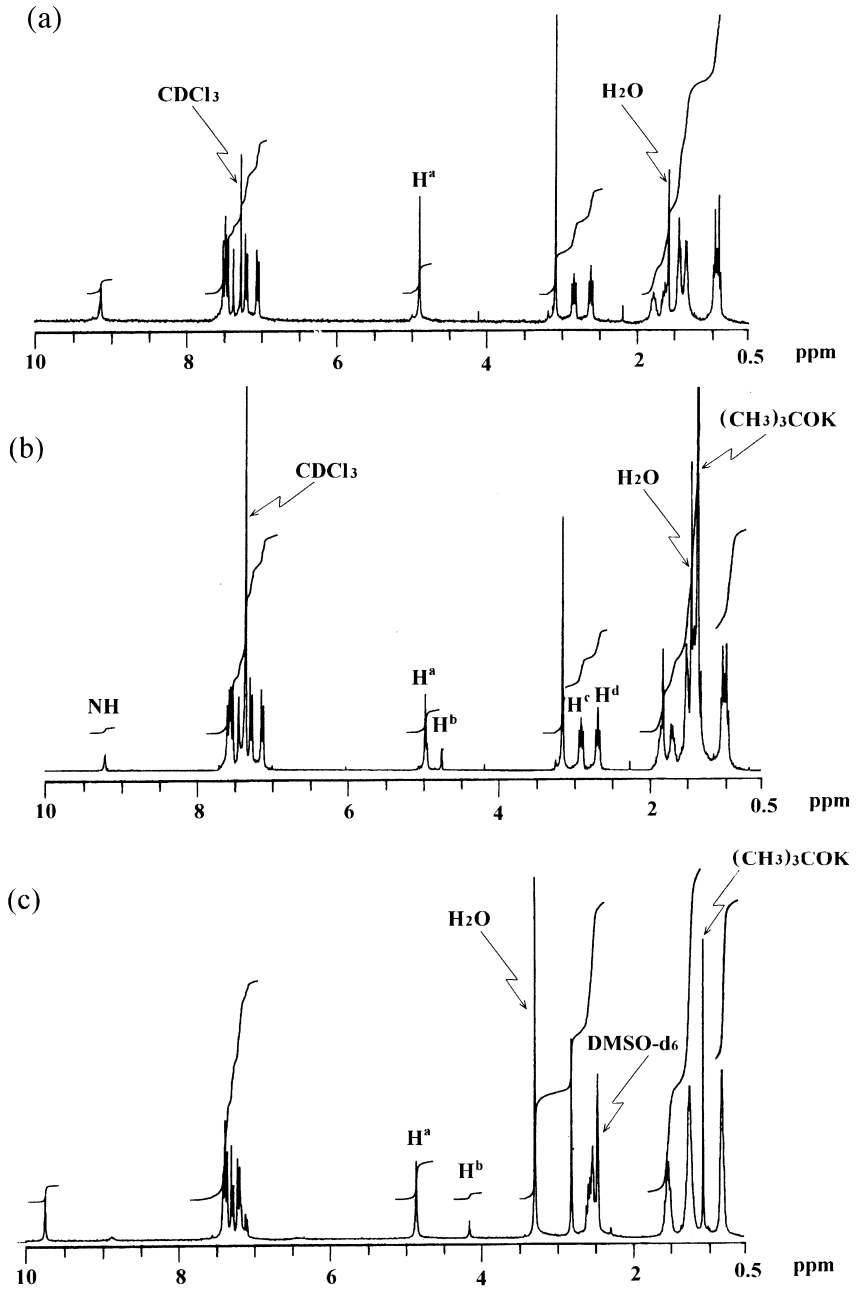
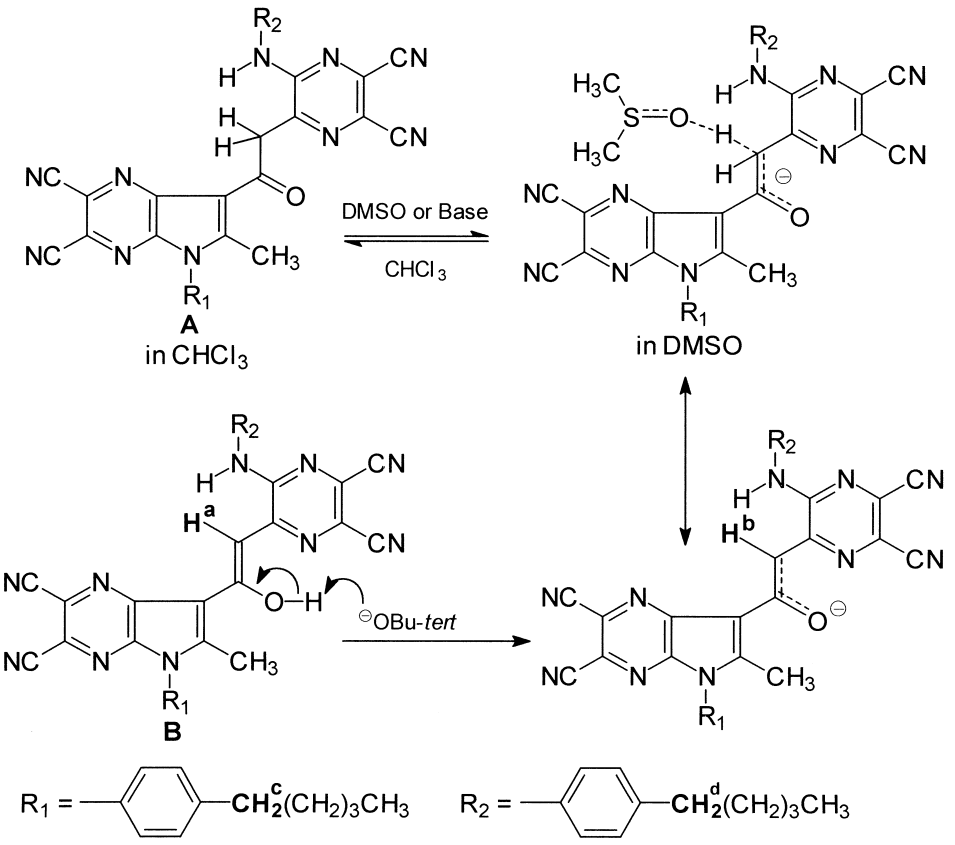


Fig. 2. 300 MHz ^{1}H-NMR spectra of **5d**; (a) in $CDCl_3$, (b) addition of potassium *tert*-butoxide to (a), (c) in DMSO-d_6 containing potassium *tert*-butoxide.

MT-3 recorder. All chemicals were reagent grade and used without further purification unless otherwise specified. 2-Amino-3-chloro-5,6-dicyanopyrazine **2** [7] was prepared by the known method.

3.1. Synthesis of **3**, **4** and **5**

Sodium hydride (0.011 mmol) dispersed in chloroform (5 cm^3) was gradually added to a solution of



Scheme 3.

2,4-pentadione (0.01 mol) in dry benzene (30 cm^3) at 15°C. After refluxing for 0.5 h, **2** (0.01 mol) was added to the reaction mixture. The flask was fitted with a Dean-Stark trap, and the mixture was refluxed for 12 h. As the reaction proceeded, **4** gradually deposited as violet precipitates, which were collected by hot filtration, washed with benzene. The crude product was poured into 2% aqueous acetic acid (100 cm^3). After stirring for 0.5 h, the mixture was extracted with ethyl acetate and dried with sodium sulfate. The solvent was removed partially in vacuo. The crude product was purified by column chromatography on silica gel using ethyl acetate/benzene (3/1) to give **4** as a purplish red solid.

The benzene filtrate was evaporated and recrystallized from ethyl acetate to give **3** as a pale yellow solid. The filtrate of **3** was concentrated. The residue was chromatographed on silica gel using ethyl acetate/benzene (1/2) to give **5** as a white solid.

3.2. *Synthesis of* **4e** *and* **5e**

Sodium hydride (0.011 mmol), dissolved in chloroform (5 cm^3), was gradually added to a solution of **3b** (0.01 mol) in dry toluene (40 cm^3) at 15°C. After refluxing for 0.5 h, **2d** (0.01 mol) was added to the reaction mixture. The flask was fitted with a Dean-Stark trap, and the mixture was refluxed for 12 h. As the reaction proceeded, **4e** gradually deposited as a violet precipitate, which was collected by hot filtration, and washed with benzene. The crude product was poured into 2% aqueous acetic acid (100 cm^3). After stirring for 0.5 h, the mixture was extracted with ethyl acetate and dried with sodium sulfate. The solvent was removed partially in vacuo. The crude product was purified by column chromatography on silica gel using ethyl acetate/benzene (3/2) to give **4e** as a purplish red solid.

The filtrate was concentrated. The residue was chromatographed on silica gel using ethyl acetate/benzene (1/2) to give **5e** as a white solid.

*3.2.1. 2,3-Dicyano-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine* **3a**

Mp: 234°C ; *m*/*z* 225 (M^+); ^{1}H NMR (DMSO-d_6) δ 2.68 (3H, s, methyl proton), 2.80 (3H, s, acetyl proton), 13.60 (1H, broad, NH).

Anal. calcd for $C_{11}H_7N_5O_1$: C, 58.67; H, 3.13; N, 31.10. Found: C, 58.35; H, 3.09; N, 30.02.

*3.2.2. 2,3-Dicyano-5-ethyl-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine* **3b**

Mp: 208°C; *m*/*z* 253 (M^+); ^{1}H NMR (DMSO-d_6) δ 1.26 (3H, t, *J* 7.2 Hz, $CH_2\mathbf{CH_3}$), 2.72 (3H, s, methyl proton), 2.94 (3H, s, acetyl proton), 4.42 (2H, q, *J* 7.2 Hz, $\mathbf{CH_2}CH_3$).

Anal. calcd for $C_{13}H_{11}N_5O_1$: C, 61.65; H, 4.38; N, 27.65. Found: C, 61.52; H, 4.43; N, 27.51.

*3.2.3. 2,3-Dicyano-5-benzyl-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine* **3c**

Mp: 188°C; *m*/*z* 315 (M^+); ^{1}H NMR ($CDCl_3$)) δ 2.73 (3H, s, methyl proton), 2.84 (3H, s, acetyl proton), 5.66 (2H, s, methylene proton), 7.16 (2H, d, *J* 10.2 Hz, phenyl proton), 7.30 (3H, m, phenyl proton).

Anal. calcd for $C_{18}H_{13}N_5O_1$: C, 68.56; H, 4.16; N, 22.21. Found: C, 68.52; H, 4.20; N, 22.08.

*3.2.4. 2,3-Dicyano-5-(4-*n*-pentylphenyl)-6-methyl-7-acetylpyrrolo[2,3-*b*]pyrazine* **3d**

Mp: 195°C; *m*/*z* 371 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.94 (3H, t, *J* 6.3 Hz, $CH_2\mathbf{CH_3}$), 1.40 (4H, m, methylene proton), 1.72 (2H, m, methylene proton), 2.75 (2H, m, methylene proton), 2.72 (3H, t, *J* 6.3 Hz, $Ph\mathbf{CH_2}$), 2.82 (3H, s, methyl proton), 2.92 (3H, s, acetyl proton), 7.23 (2H, d, *J* 8.1 Hz, phenyl proton), 7.44 (2H, d, *J* 8.1 Hz, phenyl proton).

Anal. calcd for $C_{22}H_{21}N_5O_1$: C, 71.14; H, 5.70; N, 18.85. Found: C, 71.12; H, 5.73; N, 18.81.

*3.2.5. 1-Ethyl-2-methyl-5,6-dicyano-3{2-[5-ethylamino-2,3-dicyanopyrazin-6-yl]-1-hydroxyethyl}-pyrrolo[2,3-*b*]pyrazine* **4b**

Mp > 300°C; *m*/*z* 424 (M^+); ^{1}H NMR (DMSO-d_6) δ 1.25 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 1.37 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 2.52 (3H, s, methyl proton), 3.56 (2H, t, *J* 6.9 Hz, $\mathbf{CH_2}CH_3$)), 4.30 (2H, t, *J* 6.9 Hz, $\mathbf{CH_2}CH_3$), 6.76 (1H, s, ethenyl proton), 8.07 (1H, broad, NH), 10.34 (1H, s, OH).

Anal. calcd for $C_{21}H_{16}N_{10}O_1$: C, 59.43; H, 3.80; N, 33.00. Found: C, 59.27; H, 3.93; N, 32.89.

*3.2.6. 1-Benzyl-2-methyl-5,6-dicyano-3{2-[5-benzylamino-2,3-dicyanopyrazin-6-yl]-1-hydroxyethyl}-pyrrolo[2,3-*b*]pyrazine* **4c**

Mp: 190°C; *m*/*z* 548 (M^+); ^{1}H NMR (DMSO-d_6)) δ 2.53 (3H, s, methyl proton), 4.57 (2H, d, *J* 5.1 Hz, methylene proton), 5.34 (1H, d, *J* 16.8 Hz, methylene proton), 5.67 (1H, d, *J* 16.8 Hz, methylene proton), 6.85 (1H, s, ethenyl proton), 7.31–7.55 (10H, m, phenyl proton), 8.77 (1H, broad, NH), 10.72 (1H, s, OH).

Anal. calcd for $C_{31}H_{20}N_{10}O_1$: C, 67.88; H, 3.67; N, 25.53. Found: C, 67.79; H, 3.70; N, 25.60.

*3.2.7. 1-(4-*n*-Pentylphenyl)-2-methyl-5,6-dicyano-3{2-[5-(4-*n*-pentylphenylamino)-2,3-dicyanopyrazin-6-yl]-1-hydroxyethyl}-pyrrolo[2,3-*b*]pyrazine* **4d**

Mp: 175°C; *m*/*z* 660 (M^+); ^{1}H NMR (DMSO-d_6)) δ 0.82 (6H, m, $CH_2\mathbf{CH_3}$), 1.31 (8H, m, methylene proton), 1.62 (4H, m, methylene proton), 2.51 (3H, s, methyl proton), 2.54 (2H, t, *J* 6.9 Hz, $Ph\mathbf{CH_2}$), 2.66 (2H, t, *J* 6.9 Hz, $Ph\mathbf{CH_2}$), 6.65 (1H, s, ethenyl proton), 7.15 (2H, d, *J* 8.1 Hz, phenyl proton), 7.33 (4H, m, phenyl proton), 7.53 (2H, d, *J* 8.1, phenyl proton), 9.76 (1H, broad, NH), 11.37 (1H, s, OH).

Anal. calcd for $C_{39}H_{36}N_{10}O_1$: C, 70.89; H, 5.49; N, 21.20. Found: C, 70.85; H, 5.47; N, 21.21.

*3.2.8. 1-Ethyl-2-methyl-5,6-dicyano-3{2-[5-(4-*n*-pentylphenylamino)-2,3-dicyanopyrazin-6-yl]-1-hydroxyethyl}-pyrrolo[2,3-*b*]pyrazine* **4e**

Mp > 300°C; *m*/*z* 542 (M^+); ^{1}H NMR (DMSO-d_6) δ 0.83 (6H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 1.28 (4H, m, methylene protons), 1.36 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 1.56 (2H, m, methylene protons), 2.51 (3H, s, methyl proton), 2.54 (2H, t, *J* 6.9 Hz, $Ph\mathbf{CH_2}$), 4.33 (2H, q, *J* 6.9 Hz, $N\mathbf{CH_2}$), 7.04 (1H, s, ethenyl proton), 7.22 (2H, d, *J* 8.4 Hz, phenyl proton), 7.63 (2H, d, *J* 8.4 Hz, phenyl proton), 9.64 (1H, broad, NH), 10.81 (1H, s, OH).

Anal. calcd for $C_{30}H_{26}N_{10}O_1$: C, 66.41; H, 4.83; N, 25.81. Found: C, 66.34; H, 4.80; N, 25.68.

*3.2.9. 1-Ethyl-2-methyl-5,6-dicyano-3{2-[5-ethylamino-2,3-dicyanopyrazin-6-yl]-1-oxoethyl}-pyrrolo[2,3-*b*]pyrazine* **5b**

Mp: 118°C; *m*/*z* 424 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.28 (6H, m, $CH_2\mathbf{CH_3}$), 2.99 (3H, s, methyl proton), 3.53 (2H, q, *J* 6.9 Hz, $\mathbf{CH_2}CH_3$), 4.44 (2H, q, *J* 6.9 Hz, $\mathbf{CH_2}CH_3$), 4.80 (2H, s, carbomethylene proton), 8.63 (1H, broad, NH).

Anal. calcd for $C_{21}H_{16}N_{10}O_1$: C, 59.43; H, 3.80; N, 33.00. Found: C, 59.37; H, 3.83; N, 33.10.

*3.2.10. 1-(4-*n*-Pentylphenyl)-2-methyl-5,6-dicyano-3{2-[5-(4-*n*-pentylphenylamino)-2,3-dicyanopyrazin-6-yl]-1-oxoethyl}-pyrrolo[2,3-*b*]pyrazine* **5d**

Mp: 218°C; *m*/*z* 660 (M^+); ^{1}H NMR ($CDCl_3$)) δ 0.89 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 0.94 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 1.32 (4H, m, methylene proton), 1.42 (4H, m, methylene proton), 1.62 (2H, m, methylene proton), 1.78 (2H, m, methylene proton), 2.57 (2H, t, *J* 8.1 Hz, $Ph\mathbf{CH_2}$), 2.86 (2H, t, *J* 8.1 Hz, $Ph\mathbf{CH_2}$), 3.07 (3H, s, methyl proton), 4.88 (2H, s, carbomethylene proton), 7.02 (2H, d, *J* 8.1 Hz, phenyl proton), 7.18 (2H, d, *J* 8.1 Hz, phenyl proton), 7.44 (2H, d, *J* 8.1 Hz, phenyl proton), 7.50 (2H, d, *J* 8.1 Hz, phenyl proton), 9.12 (1H, broad, NH).

Anal. calcd for $C_{39}H_{36}N_{10}O_1$: C, 70.89; H, 5.49; N, 21.20. Found: C, 70.90; H, 5.47; N, 21.16.

*3.2.11. 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**

Mp: 185°C; *m*/*z* 542 (M^+); ^{1}H NMR ($CDCl_3$) δ 0.89 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 1.22 (3H, t, *J* 6.9 Hz, $CH_2\mathbf{CH_3}$), 1.37 (4H, m, methylene proton), 1.63 (2H, m, methylene proton), 2.63 (2H, t, *J* 6.9 Hz, $Ph\mathbf{CH_2}$), 3.00 (3H, s, methyl proton), 4.78 (2H, q, *J* 6.9 Hz, $\mathbf{CH_2}CH_3$), 5.02 (2H, s, carbomethylene proton), 7.22 (2H, d, *J* 8.4 Hz, phenyl proton), 7.57 (2H, d, *J* 8.4 Hz, phenyl proton), 10.00 (1H, broad, NH).

Anal. calcd for $C_{30}H_{26}N_{10}O_1$: C, 66.41; H, 4.83; N, 25.81. Found: C, 66.42; H, 4.81; N, 25.77.

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References

[1] Webster W, Hartter DR, Begland RW, Sheppard WA, Cairncross A. Hydrogen cyanide chemistry. III. Synthesis of diiminosuccinonitrile and its conversion to diaminomaleonitrile. J Org Chem 1972;37:4133.

[2] Jaung J-Y, Matsuoka M, Fukunishi K. Syntheses and properties of new styryl dyes derived from 2,3-dicyano-5-methylpyrazines. Dyes and Pigments 1996;31:141.

[3] Jaung J-Y, Matsuoka M, Fukunishi K. Dicyanopyrazine studies. Syntheses and characterization of new bis-styryl fluorescent dyes from DAMN. Part III. Dyes and Pigments 1998;36:395.

[4] Jaung JY, Matsuoka M, Fukunishi K. Syntheses and spectral properties of dicyano-related new heterocycles from DAMN. J Res Chem 1998;284.

[5] Curphey TJ, Hung JC, Chu CCC. A study of the alkylation of enamines derived from sterically hindered amines. J Org Chem 1975;40:607.

[6] Jaung J-Y, Matsuoka M, Fukunishi K. Dicyanopyrazine studies. Part IV: syntheses and solid state absorption spectra of new dicyanopyrazine dyes derived from dichlorodicyanopyrazine and Fisher's type bases. Dyes and Pigments 1998;37:135.

[7] Jaung JY, Matsuoka M, Fukunishi K. Syntheses and spectral properties of 2,3,7,8-tetracyano-5,10-dihydrodipyrazino [2,3-*b*:2′,3′-*e*]pyrazine. Dyes and Pigments J Heterocyclic Chem 1997;34:653.