Dyes and Pigments, Vol. 37, No. 2, pp. 135–144, 1998
© 1998 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
PII: S0143-7208(97)00048-X 0143-7208/98 $19.00+0.00

Dicyanopyrazine Studies. Part IV: Syntheses and Solid State Absorption Spectra of New Dicyanopyrazine Dyes Derived from Dichlorodicyanopyrazine and Fisher's Type Bases

Jae-Yun Jaung,[a] Masaru Matsuoka[b] & Koushi Fukunishi[a]*

[a]Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan
[b]Laboratory of Material Science, Kyoto Women's University, Imakumano, Higashiyama-ku, Kyoto 605, Japan

(Received 3 April 1997; accepted 7 May 1997)

ABSTRACT

*2-Chloro-5,6-dicyano-3-[2'-(1',3',3'-trimethylindolinylidine) methyl]pyrazine **3a** showed large differences in λ_{max} from solution to solid state resulting from strong intermolecular $\pi-\pi$ interactions. Related derivatives were synthesized by the nucleophilic substitution of 2,3-dichloro-5,6-dicyanopyrazine **1** with various Fisher's base type enamines. Absorption spectra, fluorescent properties and other physical properties were correlated with their chemical structures. The Pariser–Parr–Pople molecular orbital and MOPAC approach to evaluate their absorption spectra correlate with their conformations were conducted. Good correlation between the calculated and the experimental results were obtained. The substituent effects of dicyanopyrazines affecting their chemical, electronic, and physical properties were also studied. © 1998 Elsevier Science Ltd*

Keywords: dicyanopyrazine, aminovinylpyrazine, intermolecular $\pi-\pi$ interaction, MOPAC, solid state absorption, spectra, fluorescent dye.

INTRODUCTION

2,3-Dichloro-5,6-dicyanopyrazine **1** has been the subject of intense investigation because of a wide variety of potential applications, including heterocycles for bioactive substances [1], coloring matters and so on. It has two

---

*Corresponding author.

strong electron withdrawing cyano groups on the pyrazine ring and the two chlorine atoms are very reactive to various nucleophiles. In our previous papers, we reported the reactions of **1** with amines [2] and enamines [3], and their conformational analyses were studied by means of the temperature dependence NMR spectra [3, 4] and the MOPAC method [4].

In contrast, extentions of π-conjugation by condensation reactions of the 2-methyl group of 5,6-dicyanopyrazine with arylaldehydes gave new types of fluorescent dyes [5]. Similar condensation reactions of the Wittig reagent derived from 2- and/or 3-bromomethyl-5,6-dicyanopyrazine with arylaldehydes also gave new mono- or bis-styryl pyrazine fluorescent dyes. Their absorption and fluorescent properties, correlated with molecular structures, have been reported previously [6, 7]. Ring closure reaction of 2-amino-3-chloro-5,6-dicyanopyrazine to give 2,3,7,8-tetracyano-5,10-dihydropyrazino [2,3-*b*: 2′,3′-*e*]pyrazine as new fluorescent chromophore has also been reported [8].

In this paper, we have studied the reaction of **1** with Fisher's type base to give new types of aminovinylpyrazine dyes and evaluated their spectral properties on solid state as well as in solution. Their molecular stacking behavior was also evaluated by means of the MOPAC method.

RESULTS AND DISCUSSION

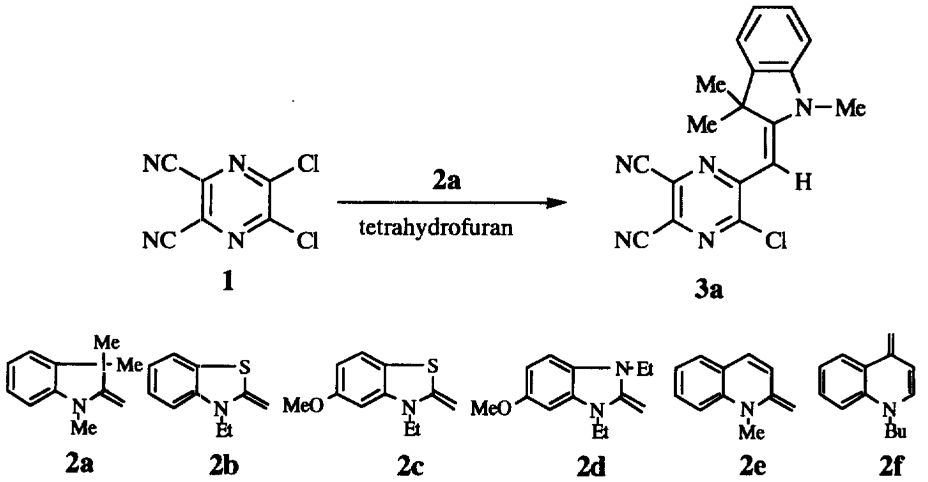
Reaction of 1 with Fisher's type base

Treatment of **1** with two equivalent of 1,3,3-trimethyl-2-methyleneindoline (**2a**) or 1-ethyl-2-methylenebezothiazoline (**2b**) in THF afforded 2-chloro-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidene)methyl]pyrazine (**3a**) in 97% yield or 2-chloro-5,6-dicyano-3-[2′-(3′-ethylbenzothiazolinylidene)methyl]-pyrazine (**3b**) in 18% yield, respectively. Related derivatives could be also obtained by using Fisher's type bases **2** as an active methylene compound. Further nucleophilic substitution of **3a** with various nuceophiles gave the desired products **4**–**8** in good yield. The results are summarized in Schemes 1 and 2 and Table 1.

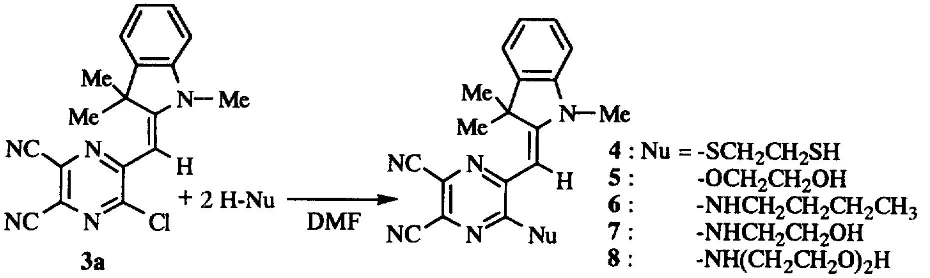
The structures of the products were confirmed by PMR, IR and mass spectra as well as microanalyses (Table 2). The stretching vibrations of the cyano groups for compounds **3a**–**3f** and **4**–**8** were observed between 2215 and 2226 cm^{-1} as a single peak in spite of their asymmetric structure.

Visible and fluorescent spectra

Visible and fluorescence spectra of dyes **3a**–**3f** and **4**–**8** in solid state and solution are summarized in Table 3. The absorption and fluorescence maxima



Scheme 1.



Scheme 2.

of these dyes in solution were observed at 427–560 nm and 496–540 nm, respectively. The electronic character of the substituents in dyes **3a**–**3f** strongly affect their absorption spectra, producing bathochromic shifts depending both on the basicity of the heterocyclic moiety and the enlargement of the π-conjugated systems.

Dye **3a** absorbed at 472 nm in chloroform and dyes **3b** and **3c** absorbed at similar wavelength region, but dye **3d** showed a hypsochromic shift of 45 nm caused by the steric hindrance of the *N*-ethyl groups against the pyrazine moiety. The small ε value of dye **3d** indicated the steric requirement of the *N*-ethyl groups. The quinoline analogues (**3e** and **3f**) produced a large bathochromic shift of 60–90 nm compared to dye **3a**, due to enlargement of the π-conjugation system, and **3f** absorbed at much longer wavelength than **3e**.

TABLE 1
Reaction of **1** and Enamines[a], and Nucleophilic Substitution of **3a**[b]

Run	*Reactant*	*Reagent*	*Time (h)*	*Product*	*Yield (%)*
1	**1**	2a	2	**3a**	97
2	**1**	2b	2	**3b**	18
3	**1**	2c	2	**3c**	17
4	**1**	2d	2	**3d**	10
5	**1**	2e	2	**3e**	86
6	**1**	2f	2	**3f**	53
7	**3a**	$HSCH_2CH_2SH$	4	**4**	56
8	**3a**	$HOCH_2CH_2OH$	6	**5**	62
9	**3a**	$NH_2CH_2CH_2CH_2CH_3$	3	**6**	60
10	**3a**	$NH_2CH_2CH_2OH$	3	**7**	52
11	**3a**	$NH_2(CH_2CH_2O)_2H$	5	**8**	54

[a] A mixture of **1** (10 mmol) and enamine (20 mmol) in tetrahydrofuran (20 ml) was stirred at room temperature (Runs 1–6).
[b] A mixture of **3a** (2 mmol) and nucleophile (4 mmol) was stirred at 40°C (Runs 7–11).

In contrast, the λ_{max} values of dyes **3a**–**3f** in solid state changed drastically with the differences in the molecular stacking of each dye, which was evaluated by the $\Delta\lambda$ values. Dyes **3a** and **3f** have large $\Delta\lambda$ values of 113 nm and 59 nm, respectively (Fig. 1), but dyes **3b** and **3c** showed negative $\Delta\lambda$ values, which indicated a hypsochromic shift of λ_{max} from solution to solid state. It is generally known that the λ_{max} of dyes in solid state shift to longer wavelength compared with in solution, resulting from stronger intermolecular $\pi-\pi$ interactions of dye molecules in solid state. In contrast, hypsochromic shifts caused by dye aggregation are well known in cyanine dyes, in which cancellation of the dipole moment was observed in the dimer.

It was calculated that dyes **3a**–**3f** have a strong intramolecular charge-transfer chromophoric system, and dyes **3b** and **3c** have a planar molecular

TABLE 2
Analytical Data for Dyes **3a**–**8**

Compd.	*Formula*	*mp (°C)*	*Calcd. (Found, %)* C	H	N
3a	$C_{18}H_{14}N_5Cl$	282–284	64.38 (63.98)	4.20 (4.23)	20.85 (20.57)
3b	$C_{16}H_{10}N_5SCl$	> 300	56.55 (55.91)	2.95 (3.06)	20.62 (20.51)
3c	$C_{17}H_{12}N_5OSCl$	286–288	55.20 (54.78)	3.25 (3.31)	18.94 (18.74)
3d	$C_{19}H_{17}N_6OCl$	217–218	59.92 (59.83)	4.47 (4.55)	22.08 (21.70)
3e	$C_{17}H_{10}N_5Cl$	261–262	63.85 (63.80)	3.13 (3.14)	21.91 (21.58)
3f	$C_{20}H_{16}N_5Cl$	256–257	66.39 (66.23)	4.43 (4.52)	19.36 (19.09)
4	$C_{20}H_{19}N_5S_2$	185–186	61.04 (60.87)	4.87 (4.79)	17.80 (17.27)
5	$C_{20}H_{19}N_5O_2$	> 300	66.47 (66.14)	5.30 (5.39)	19.38 (19.19)
6	$C_{22}H_{24}N_6$	193–194	70.94 (70.52)	6.49 (6.46)	22.56 (22.42)
7	$C_{20}H_{20}N_6O$	223–224	66.65 (66.21)	5.59 (5.43)	23.32 (22.94)
8	$C_{22}H_{24}N_6O_2$	165–166	65.33 (64.92)	5.98 (6.08)	20.78 (20.43)

TABLE 3
Visible and Fluorescence Spectra of Dyes **3**–**8**

Compd.	λ_{max} *(nm)* *$CHCl_3$(log ε)*	*Solid*[a]	$\Delta\lambda$[b] *(nm)*	F_{max} *(nm)* *$CHCl_3$*[c]	*Solid*[d]	ΔF[e] *(nm)*	*Ss*[f] *(nm)*
3a	472 (4.58)	585	113	540	625	85	68
3b	463 (4.62)	395	−68	—	—	—	—
3c	473 (4.75)	447	−26	—	—	—	—
3d	427 (4.32)	437	10	—	—	—	—
3e	536 (4.43)	515	−21	—	—	—	—
3f	560 (4.91)	619	59	—	—	—	—
4	470 (4.46)	489	19	527	630	103	57
5	464 (4.40)	527	63	512	568	56	48
6	462 (4.61)	490	28	496	590	94	34
7	465 (4.56)	494	29	502	582	80	37
8	462 (4.55)	492	30	508	573	65	46

[a] Vapor deposited thin film.
[b] $\Delta\lambda = \lambda_{max}$ (solid) − λ_{max} ($CHCl_3$).
[c] Fluorescence maximum excited at λ_{max} value.
[d] Solid state fluorescence maximum excited at 360 nm.
[e] $\Delta F = F_{max}$ (solid)$-F_{max}$(soln.).
[f] Stoke's shift.

structure because of the absence of steric hindrance of the sulfur atom in the thiazole ring compared with those in dyes **3a** and **3d**.

Dyes **4**–**8** absorbed at around 465 nm which indicated that the electron donating substituent at the 3-position of dye **3a** did not affect on their λ_{max} value. These observations were well evaluated by the PPP MO method in which π-electron density change accompanying the first excitation was rather small at the 3-position. The $\Delta\lambda$ values of dyes **4**–**8** were almost the same (20–30 nm), except for dye **5** which showed a large $\Delta\lambda$ value of 63 nm. Again, this was caused by the special molecular stacking of dye **5** in solid state. It is not obvious why only dye **5** showed such a large $\Delta\lambda$ value, in spite of its structural similarity to the other dyes.

Dye **3a** has fluorescence in solution and on solid state, but dyes **3b**–**3f** did not show any fluorescence. These phenomena are not yet understood, but are under investigation by using molecular orbital calculations. Dyes **4**–**8** derived from dye **3a** had fluorescence both in solution and solid state. The ΔF value, indicating the difference in F_{max} from solid state to solution, changed largely from 56 nm of dye **5** to 103 nm of dye **4**. It is of interest to note that dye **3a** showed green fluorescence in solution, but red fluorescence in solid state. Similar results were also observed in the cases of dyes **4** and **5**. It is well known that the Stoke's shift indicates the degree of stabilization in the excited state of a dye molecule, and a large ΔF value indicates large stabilization of the excited state in solid state compared with that in solution. From these results, both $\Delta\lambda$ and ΔF values will be a measure of an effective molecular

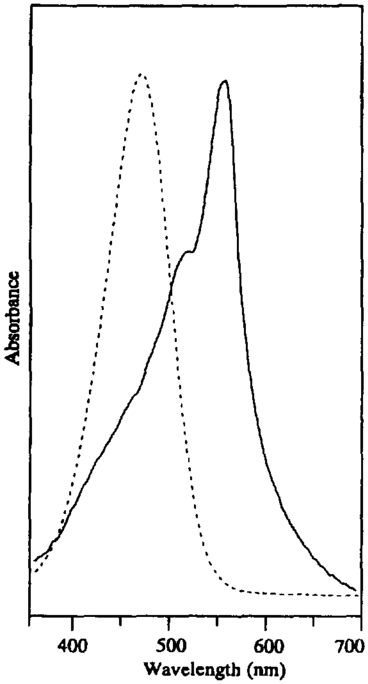
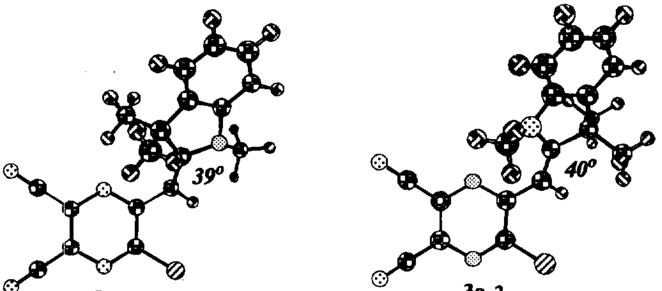


Fig. 1. Differences in absorption spectra of **3a** in chloroform (----) and vapor deposited thin film (——).

stacking caused by intermolecular $\pi-\pi$ interactions in solid state. The quantitative explanation of these $\pi-\pi$ interactions will be correlated by the X-ray crystal analysis data of these dyes in due course.

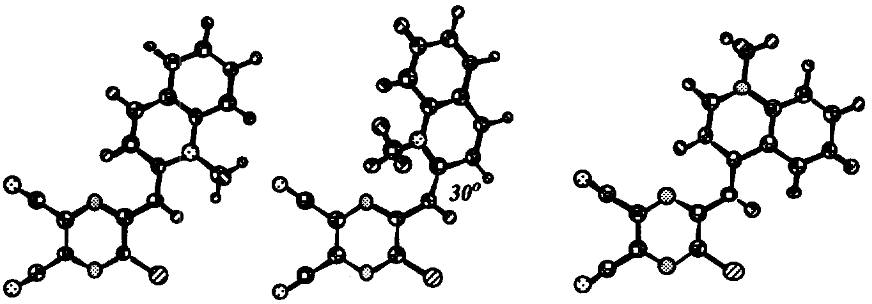
Conformation analysis by MOPAC PM 3 method

The optimized molecular structure of dye **3a** was evaluated by using the MOPAC PM 3 method. As indicated before, some steric hindrances between the *N*-methyl or the isopropyl groups and the lone pair electron of the pyrazine ring were proposed. Two conformers shown in Fig. 2 were obtained as the optimized structure of dye **3a**. Both structures have a bent structure between two π-ring systems and their dihedral angles were almost the same, viz., 39° and 40°, respectively. From the results of the calculated heat of formation (ΔHf), **3a-1** is more stable than **3a-2**. Dye **3a** has a smaller ε value compared with that of dye **3b**, which was caused by the twisted π-conjugation of dye **3a**. In the case of dye **3e**, **3e-1** has a much smaller ΔHf value than **3e-2**, and **3e-2** showed a dihedral angle of 30° because of the steric hindrance of the *N*-methyl group with the nitrogen lone pair. As a conclusion, dye **3e** exists as the structure **3e-1**, which has a planar π-conjugation system with a smaller ΔHf value.



3a-1
ΔHf = 143.03 kcal/mol

3a-2
ΔHf = 141.67 kcal/mol



3e-1
ΔHf = 162.72 kcal/mol

3e-2
ΔHf = 167.70 kcal/mol

3f (R=Me)
ΔHf = 163.70 kcal/mol

Fig. 2. Evaluations of the optimized structures of dyes **3a**, **3e** and **3f** by MOPAC PM 3 method.

The optimized structure for dye **3f**, calculated as the *N*-methyl derivative, was confirmed as **3f**(R = Me) shown in Fig. 2, and has a ΔHf of 163.7 kcal mol^{-1} and a completely planar π-conjugated structure. Dye **3f** absorbed at the longest wavelength of 560 nm and has the largest ε value, which is due to the most effective π-conjugation without any steric hindrances.

Molecular stacking behaviors of these dyes by using the optimized molecular structures will be evaluated from the points of intermolecular $\pi-\pi$ interactions by means of molecular dynamics (MD) simulations together with X-ray crystal analysis.

Experimental

Identifications of compounds and measurements of properties were carried out by general procedures using the following equipment. Melting points were determined on a Yanagimoto micro melting point apparatus without correction. The PMR spectra were taken on an FT-NMR QE 300 MHz Shimadzu spectrometer. The MS spectra were recorded on an M-80 B Hitachi mass spectrometer. The visible and fluorescence spectra were measured on a U-3410 Hitachi spectrophotometer and Shimadzu RF-5000 fluorescence spectrophotometer respectively. Microanalysis was conducted with a Yanaco CHN MT-3 recorder. All chemicals were reagent grade and used without further purification unless otherwise specified.

Syntheses of 3a–3f

To a solution of **1** (0.50 g, 2.5 mmol) in tetrahydrofuran (15 ml) was added dropwise **2a–2f** (5 mmol), and the mixture was then stirred at room temperature until all **1** had reacted on tlc (see Table 1 for reaction time). The reaction mixture was poured into 70 ml of water. The precipitate was filtered, washed with water and dried, to give the crude product **3a–3f**.

2-Chloro-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidene)methyl]pyrazine (3a)

The crude product was recrystallized from acetonitrile to give **3a** as a red solid in 97% yield, IR: ν CN 2218 cm^{-1}; ms: *m/z* 337 ([M + 2]$^+$), 335 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 7.36–6.89 ((*t* + *t* + *d* + *d*), 4H, phenyl protons), 5.91 (s, 1H, -CH=), 3.42 (s, 3H, NCH$_3$), 1.82(s, 3H, CH$_3$), 1.55(s, 3H, CH$_3$).

2-Chloro-5,6-dicyano-3-[2′-(3′-ethylbenzothiazolinylidene)methyl]pyrazine (3b)

The crude product was purified by column chromatography on silica gel using chloroform as eluent and was recrystallized from ethyl acetate/cyclohexane, giving **3b** as orange crystals (18%), IR: ν CN 2223 cm^{-1}; ms: *m/z* 341 ([M + 2]$^+$), 339 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 7.80–7.33 ((*d* + *d* + *t* + *t*), 4H, phenyl protons), 6.38 (s, 1H, -CH=), 4.36 (q, 2H, NCH$_2$), 1.34(t, 3H, CH$_3$).

2-Chloro-5,6-dicyano-3-[2′-(3′-ethyl-5′-methoxybenzothiazolidene)methyl]-pyrazine (3c)

The crude product was purified by column chromatography on silica gel using chloroform as eluent and was recrystallized from ethyl acetate/cyclohexane, giving **3c** as orange crystals (17%), IR: ν CN 2218 cm^{-1}; ms: *m/z* 371 ([M + 2]$^+$), 369 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 7.65–6.84 ((*d* + *d* + *s*), 3H, phenyl protons), 6.36 (s, 1H, -CH=), 4.28 (q, 2H, NCH$_2$), 3.92 (s, 3H, OCH$_3$) 1.48(t, 3H, CH$_3$).

2-Chloro-5,6-dicyano-3-[2′-(1′,3′-diethyl-5′-methoxybenzoimidazolinylidene) methyl]pyrazine (3d)

The crude product was recrystallized from acetonitrile to give **3d** as a red solid in 10% yield, IR: ν CN 2219 cm^{-1}; ms: *m/z* 382 ([M + 2]$^+$), 380 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 7.34–6.89 ((*d* + *d* + *s*), 3H, phenyl protons), 5.13 (s, 1H, -CH=), 4.24 (q, 4H, CH$_2$), 3.91 (s, 3H, OCH$_3$), 1.50(t, 6H, CH$_3$).

2-Chloro-5,6-dicyano-3-[2′-(1′-methylquinolinylidene)methyl]pyrazine (3e)

The crude product was recrystallized from acetonitrile to give **3e** as a brown solid in 86% yield, IR: ν CN 2219 cm^{-1}; ms: m/z 321 ([M+2]$^+$), 319 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 7.76–7.38 ((d+d+t+t+m), 6H, phenyl protons), 5.99 (s, 1H, -CH=), 3.82 (s, 3H, OCH$_3$).

*2-Chloro-5,6-dicyano-3-[4′-(1′-*n*-butylquinolinylidene)methyl]pyrazine (3f)*

The crude product was recrystallized from acetonitrile to give **3f** as a brown solid in 53% yield, IR: ν CN 2216 cm^{-1}; ms: m/z 363 ([M+2]$^+$), 361 (M$^+$); ^{1}H NMR (CDCl$_3$): δ 8.62–7.49 ((d+d+t+m), 6H, phenyl protons), 6.85 (s, 1H, -CH=), 4.24 (t, 2H, CH$_2$), 1.90 (quin, 2H, CH$_2$), 1.45 (m, 2H, CH$_2$), 1.01(t, 3H, CH$_3$).

Syntheses of ***4–8***. To a solution of **3a** (0.67 g, 2.0 mmol) in *N*,*N*-dimethylformamide (10 ml) was added dropwise the appropriate nucleophile (4 mmol) at room temperature, and then the mixture was stirred at 40–45°C until all **3a** disappeared on tlc (see Table 1 for reaction time). The reaction mixture was poured into 70 ml of water. The precipitate was filtered, washed with water and dried, to give the crude product **4–8**.

2-(2′-Mercaptoethylthio)-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidene)methyl]pyrazine (4)

The crude product was recrystallized from ethyl acetate/cyclohexane to give **4** as a red solid in 56% yield, IR: ν CN 2226 cm^{-1}; ms: m/z 393 (M$^+$), 346 (M$^+$-CH$_2$SH); ^{1}H NMR (CDCl$_3$): δ 7.34–6.89 (m, 4H, phenyl protons), 5.41 (s, 1H, -CH=), 3.66 (t, 2H, CH$_2$), 3.44 (t, 2H, CH$_2$), 3.39 (s, 3H, NCH$_3$),1.82(s, 3H, CH$_3$), 1.48(s, 3H, CH$_3$).

2-(2′-Hydroxyethoxy)-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidene)methyl]pyrazine (5)

The crude product was recrystallized from ethyl acetate to give **5** as an orange solid in 62% yield, IR: ν CN 2216 cm^{-1}; ms: m/z 361 (M$^+$), 330 (M$^+$-CH$_2$OH); ^{1}H NMR (CDCl$_3$): δ 7.31–6.89 (m, 4H, phenyl protons), 5.86 (s, 1H, -CH=), 4.57 (t, 2H, CH$_2$), 4.08 (t, 2H, CH$_2$), 3.41 (s, 3H, NCH$_3$),1.83(s, 3H, CH$_3$), 1.48(s, 3H, CH$_3$).

*2-(*n*-Butylamino)-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidine)methyl]pyrazine (6)*

The crude product was recrystallized from ethyl acetate/cyclohexane to give **6** as an orange solid in 60% yield, IR: ν CN 2222 cm^{-1}; ms: m/z 372 (M$^+$), 329 (M$^+$-CH$_2$CH$_2$CH$_3$); ^{1}H NMR (CDCl$_3$): δ 7.30–6.76 (m, 4H, phenyl protons), 5.33 (br s, 1H, NH), 4.90 (d, 1H, -CH=), 3.57 (t, 2H, CH_2),3.30 (d, 3H, NCH_3),1.75(s, 3H, CH_3), 1.68 (m, 2H, CH_2), 1.46(s, 3H, CH_3), 1.43 (m, 2H, CH_2), 0.99 (t, 3H, CH_3).

2-(2′-Hydroxyethyamino)-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidine) methyl]pyrazine (7)

The crude product was recrystallized from ethyl acetate to give **7** as an orange solid in 52% yield, IR: ν CN 2223 cm^{-1}; ms: m/z 360 (M^+), 329 (M^+-CH_2OH); ^1H NMR ($CDCl_3$): δ 7.33–6.77 (m, 4H, phenyl protons), 5.82 (br s, 1H, NH), 5.01 (d, lH, -CH=), 3.92 (d, 2H, CH_2), 3.72 (d, 2H, CH_2), 3.27 (d, 3H, NCH_3),1.76(s, 3H, CH_3), 1.46(s, 3H, CH_3).

2-(2′-Hydroxyethoxyethylamino)-5,6-dicyano-3-[2′-(1′,3′,3′-trimethylindolinylidine)methyl]pyrazine (8)

The crude product was recrystallized from ethyl acetate/cyclohexane to give **8** as an orange solid in 54% yield, IR: ν CN 2221 cm^{-1}; ms: m/z 404 (M^+), 373 (M^+-CH_2OH); ^1H NMR ($CDCl_3$): δ 7.33–6.77 (m, 4H, phenyl protons), 5.89 (br s, 1H, NH), 5.01 (d, 1H, -CH=), 3.75 (d, 6H, CH_2), 3.64 (m, 2H, CH_2), 3.31 (d, 3H, NCH_3),1.76 (s, 3H, CH_3), 1.45 (s, 3H, CH_3).

REFERENCES

1. Nakamura, A., Ataka, T., Segawa, H., Takeuchi, Y. and Takematsu, T., *Agricultural and Biological Chemistry*, 1983, **47**, 1555.
2. Hou, D. and Matsuoka, M., *Dyes and Pigments*, 1993, **22**, 57.
3. Hou, D., Oshida, A. and Matsuoka, M., *Journal of Heterocyclic Chemistry*, 1993, **30**, 1571.
4. Shiozaki, H., Oshida, A., Hou, D. and Matsuoka, M., *Dyes and Pigments*, 1997, **33**, 33.
5. Jaung, J. Y., Matsuoka, M. and Fukunishi, K., *Dyes and Pigments*, 1996, **31**, 141.
6. Jaung, J. Y., Matsuoka, M. and Fukunishi, K., *Dyes and Pigments*, 1997, **34**, 255.
7. Jaung, J. Y., Matsuoka, M. and Fukunishi, K., *Dyes and Pigments*, 1997, **34**, 395.
8. Jaung, J. Y., Matsuoka, M. and Fukunishi, K., *Journal of Heterocyclic Chemistry*, 1997, **34**, 653.