

# New syntheses and solid state fluorescence of azomethine dyes derived from diaminomaleonitrile and 2,5-diamino-3,6-dicyanopyrazine

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Dedicated to Dr. Arnold T. Peters on the occasion of his retirement

## Abstract

New fluorescent dyes of interest as red light emitters for electroluminescence devices were synthesized by the condensation of diaminomaleonitrile and 2,5-diamino-3,6-dicyanopyrazine with arylaldehydes. Substituent effects on their absorption and fluorescence spectra in the solution were determined by comparison with the parent chromophoric system. Their solid state absorption and fluorescence properties were evaluated with respect to their optimized molecular structures obtained by MOPAC methods. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** 2,5-Diamino-3,6-dicyanopyrazine; Bisazomethine fluorescent dye; New fluorescent chromophore; Solid state fluorescence; Fluorescence quenching; EL emitter

## 1. Introduction

Fluorescent dyes are currently of great interest in various application fields such as emitters for electroluminescence (EL) devices [1], copy-preventing inks, solar energy collecting materials, fluorescent film for agricultural purposes, and fluorescent materials.

It is very important to design and develop new fluorescent chromophores which have special functionalities as new dye materials. We intend to use diaminomaleonitrile and 2,5-diamino-3,6-

dicyanopyrazine as sources of new fluorescent chromophores especially for use as red light emitters in EL devices. We have described the chemistry of a series of pyrazine dyes and have correlated their absorption and fluorescence properties with their molecular stacking [2]. Except for our research, few pyrazine derivatives have been reported as dye chromophores [3], but cyanopyrazines derived from diaminomaleonitrile and diiminosuccinonitrile have been extensively studied by Du Pont groups [4].

We have recently reported that pyrazine-containing dyes show strong fluorescence with high quantum yield [5], and we intend to develop new fluorescent pyrazine dyes to correlate their functionalities with structures at molecular and aggregate

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levels. Molecular design of new dye chromophores can be performed by using various molecular orbital (MO) methods and the optimized molecular structures simulated by molecular mechanics (MM) methods. These computational methodologies can assist in the design of these new functional dye materials. Material design of dye aggregates such as single crystals and vapor deposited thin films is very difficult because the evaluation of intermolecular interactions of dye chromophores in aggregates is poorly developed [2]. On the other hand, many functionalities of dye materials such as electroluminescence, photoconductivity, photovoltaic efficiency and nonlinear optical susceptibility depend largely on the intermolecular  $\pi-\pi$  interactions of the chromophores, simulation of which is possible by molecular dynamics procedures.

In this paper, we describe the synthesis of novel bisazomethine fluorescent dyes from the reaction of diaminomaleonitrile and 2,5-diamino-3,6-dicyanopyrazine with arylaldehydes. Their visible and fluorescence spectra in solution and in the solid state are correlated with their optimized molecular structures. Some dyes evaluated as emitters for the EL devices exhibit orange to red light emission from the devices. Fluorescence quenching and spectral shifts from the solution to the solid state are correlated with the molecular stacking behaviour and the intermolecular  $\pi-\pi$  interactions of the dyes.

## 2. Results and discussion

### 2.1. Syntheses of azomethine dyes derived from diaminomaleonitrile and 2,5-diamino-3,6-dicyanopyrazine with arylaldehydes

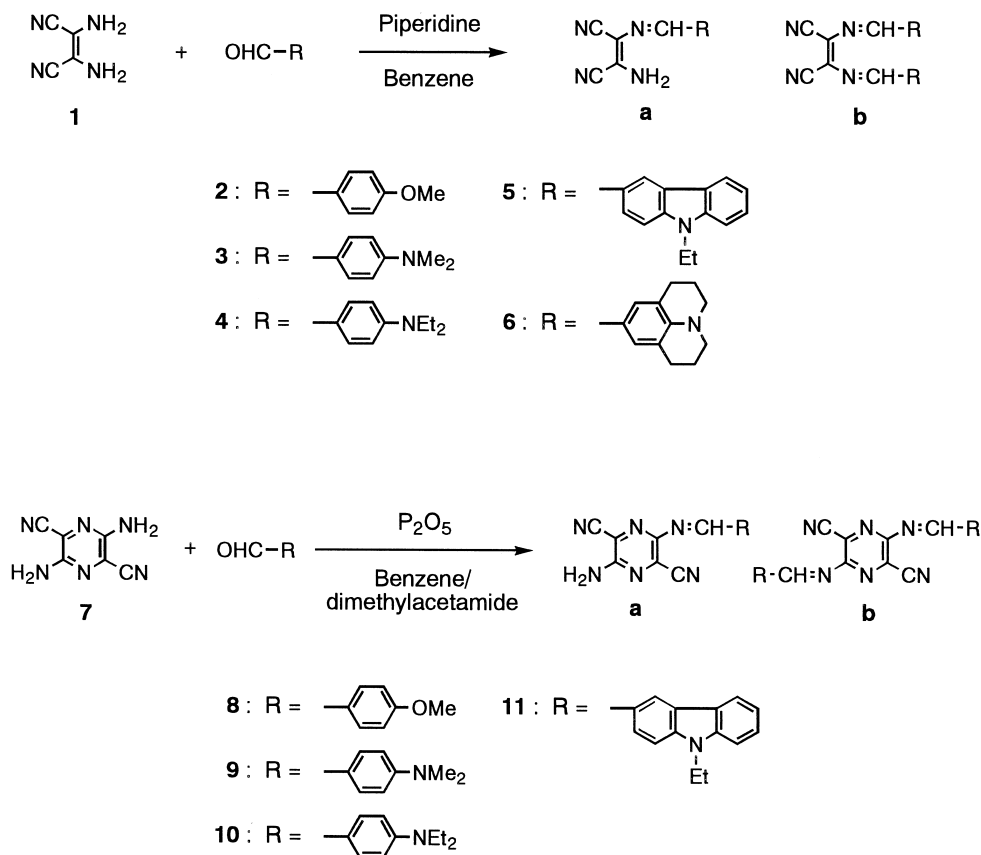
It is well known that the amino groups of diaminomaleonitrile (**1**) react with carbonyl groups to afford azomethine linkages. The reaction of **1** with 1,2-dicarbonyl compounds gives pyrazine derivatives [6] and with 1,3-dicarbonyl compound diazepine derivatives are produced [4,7]. These products are valuable intermediates for the syntheses of new fluorescence chromophores [2]. Bis-azomethine dyes derived from diaminomaleonitrile with

arylaldehydes are known in the patent literature [8] and are reported as bright and tinctorial disperse dyes for polyester and polyester-cotton blend fibres dyeing in yellow to blue shades, but none of their fluorescence properties were described. The condensation of **1** with arylaldehydes proceeded in the presence of base in benzene, removing the generated water with a Dean–Stark trap. Mono- and bis-azomethine dyes can be synthesized by changing the molar ratio of the reactants. In the case of the reaction of **1** with 3-formyl-*N*-ethylcarbazole, only the bis-substituted product (**5b**) was obtained under various conditions.

The condensation of 2,5-diamino-3,6-dicyanopyrazine (**7**) with arylaldehydes gave 2,5-bis[(arylmethylidene)amino]-3,6-dicyanopyrazines together with their mono-substituted analogues in all cases. The reaction was carried out in a mixture of benzene and dimethylacetamide in the presence of diphosphorous pentoxide. The results are summarized in the experimental section. The reactions of **1** or **7** with arylaldehydes, and the products are detailed in Scheme 1. The optimized molecular structures of the products were calculated by using MOPAC and their structures are summarized in Fig. 1. All of the other conformers with respect to the azomethine linkage of the corresponding dyes resulted in unfavorable heats of formation. Bis-azomethine dyes derived from **1** and arylaldehydes have a large dipole moment at the molecular level. They have a completely planar  $\pi$ -system by the AM1 method but some bent structure is indicated by the PM3 method. On the other hand, bis-azomethine dyes derived from **7** have no dipole moment at the molecular level and have completely planar structures by both AM1 and PM3 methods. From these observations, the two parent chromophores appear to have planar structures which can be expected to lead to strong intermolecular  $\pi-\pi$  interactions in the solid state.

### 2.2. Visible and fluorescence spectra

The molecular orbital [5] and molecular mechanics calculation results revealed that these chromophores have a strong intramolecular charge-transfer chromophoric system and have quite a planar  $\pi$ -conjugation system. Introduction of an electron



Scheme 1.

donating substituent in the aryl moiety produces a bathochromic shift of the absorption maximum ( $\lambda_{\text{max}}$ ) together with an increase  $\epsilon_{\text{max}}$ . Substituent effects on their absorption and fluorescence spectra in the solution and the solid states are summarized in Table 1.

In a series of mono-azomethine dyes (**2a–6a**), the  $\lambda_{\text{max}}$  value in chloroform exhibited a bathochromic shift depending on the electron donating ability of the substituent from the methoxy group (**2a**) to the julolidine derivative (**6a**). Substituent effects are denoted by the  $\delta\lambda$  value which increases in the order **6a** > **4a** > **3a** > **2a**. The fluorescence maximum ( $F_{\text{max}}$ ) in chloroform and  $\delta F$  values showed similar substituent effects with **6a** emitting at the longest wavelength (517 nm) in the series. The  $\epsilon_{\text{max}}$  value increases in the order **4a** > **6a** > **3a** > **2a**. On the other hand, bis-azomethine

dyes (**2b–6b**) showed two absorption maxima for the first band. From the results of MOPAC calculations (Fig. 1), it is proposed that these dyes have two cross-conjugated donor–acceptor systems at the central ethylene moiety, and separation of the degenerated first excitation (AM1) or the separated two transitions with small energy difference due to molecular unsymmetry (PM3) probably gave the double-headed absorption bands. Bis-azomethine dyes showed a large bathochromic shift compared with the corresponding mono-azomethine dyes. The  $\delta\lambda$  values of **3b–6b** are significantly larger than those of **3a–6a** and the  $\epsilon_{\text{max}}$  values are 2–2.7 times greater than those of the corresponding mono-azomethine dyes. It is noteworthy that simple bis-azomethine dyes **3b** and **4b** showed very large  $\epsilon_{\text{max}}$  values over 100,000. From these results, the strong intramolecular

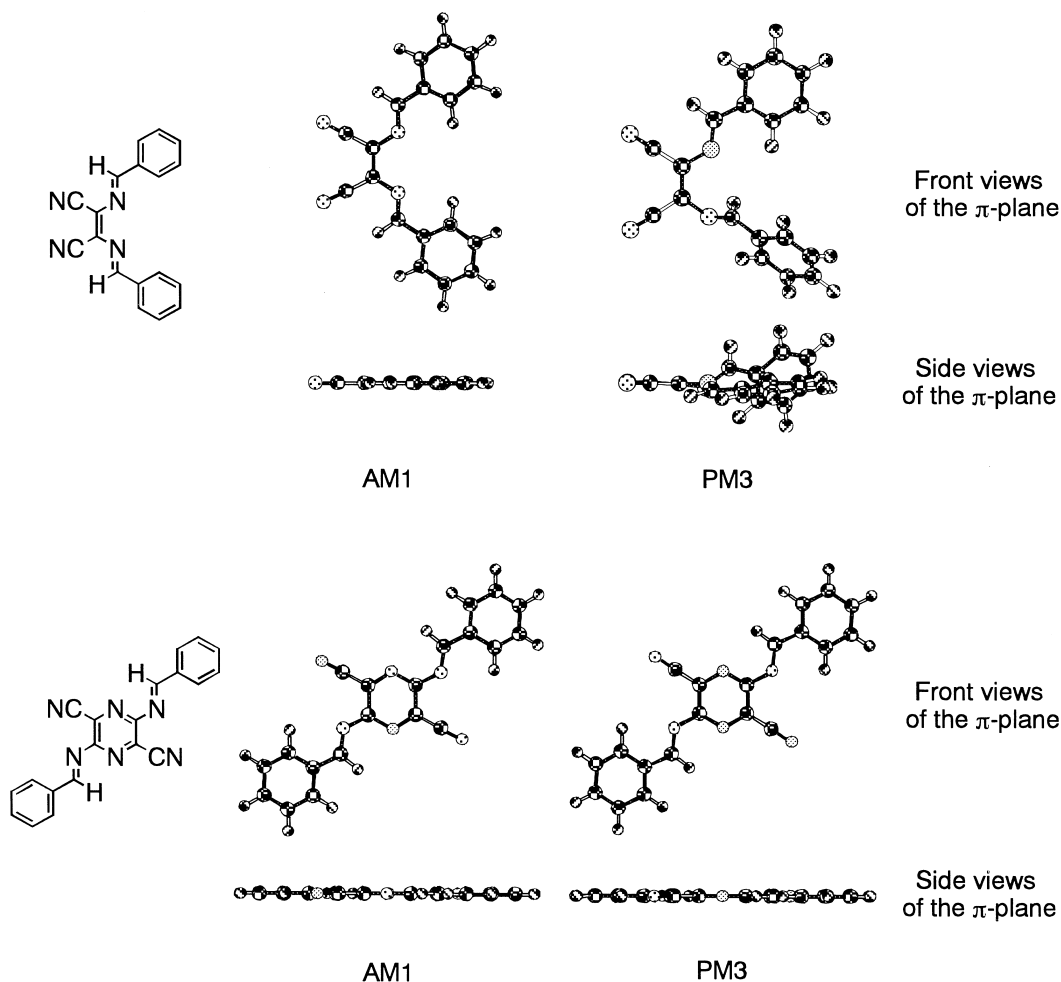


Fig. 1. Optimized molecular structures of the basic chromophores of bis-azomethine dyes by MOPAC AM1 and PM3 methods.

charge-transfer chromophoric systems of these azomethine dyes were confirmed. Their  $F_{\max}$  values shifted to a much longer wavelength region compared to the corresponding mono-azomethine dyes and **6b** emitted red fluorescence at 620 nm, which shows promise as a red light emitting material for EL devices. The Stokes shift (SS) values for these dyes are in the range of 43–65 nm and are rather small in comparison with those (80–120 nm) of 2,5-bis(*N,N*-dialkylamino)-3,6-dicyanopyrazines [5].

In the case of solid state absorption and fluorescence spectra,  $\delta\lambda$  and  $\Delta F$  values denote the spectral shift from the solid state to the solution,

respectively. These values are considered to be an indicator of molecular stacking or intermolecular  $\pi-\pi$  interactions of the chromophores [2]. Dyes **3a** and **4b** showed large  $\Delta\lambda$  values of around 60 nm but those of the others are in the range 20–40 nm. Dyes **3a**, **4a**, **3b** and **4b** showed  $\Delta F$  values of over 100 nm which are lead to longer wavelength emission in the orange to red light region. In practice, **3b** and **5b** showed quite strong red fluorescence, but **4b** showed only weak red fluorescence in the solid state. The relative strength of fluorescence in the solid state is measured in the powder state and **3a**, **3b** and **5b** showed strong fluorescence but the others are generally weak in the solid state. Solid

Table 1  
Substituent effects on the absorption and fluorescence spectra of azomethine dyes (**2–6**) in solution and in the solid state

Dye no.	$\lambda_{\max}$ (nm) <sup>a</sup>	$\delta\lambda^b$	$\varepsilon_{\max}$	$F_{\max}^a$ (nm)	$\delta F^c$	SS <sup>d</sup> (nm)	$\lambda_{\max}$ (nm) <sup>e</sup>	$\Delta\lambda^f$	$F_{\max}^g$ (nm)	$\Delta F^h$	R.I. <sup>i</sup>
<b>2a</b>	371	–	33,900	436	–	65	407	36	– <sup>j</sup>	–	–
<b>3a</b>	428	57	45,200	479	43	51	491	63	582	103	46,600
<b>4a</b>	438	67	51,100	487	51	49	469	31	605	118	2600
<b>6a</b>	456	85	48,800	517	81	61	477	21	542	25	300
<b>2b</b>	423	–	69,300	485	–	62	472	28	– <sup>j</sup>	–	–
	444		62,900								
<b>3b</b>	502s	91	86,300	583	98	48	574	39	692	109	17,200
	535		122,000								
<b>4b</b>	512s	102	76,700	590	105	44	607	61	705	115	1200
	546		118,000								
<b>5b</b>	475s	59	74,700	546	61	43	537	34	620	74	10,100
	503		92,500								
<b>6b</b>	536s	130	58,300	620	135	46	609	35	– <sup>j</sup>	–	–
	574		99,100								

<sup>a</sup> Measured in chloroform.

<sup>b,c</sup> Substituent effects in  $\lambda_{\max}$  and  $F_{\max}$ , respectively.

<sup>d</sup> Stokes shift,  $F_{\max} - \lambda_{\max}$  in solution.

<sup>e</sup> Measured in the vapor deposited thin film.

<sup>f</sup>  $\Delta\lambda = \lambda_{\max}(\text{solid}) - \lambda_{\max}(\text{solution})$ .

<sup>g</sup> Measured in the powder state.

<sup>h</sup>  $\Delta F = F_{\max}(\text{solid}) - F_{\max}(\text{solution})$ .

<sup>i</sup> Relative intensity of fluorescence in the powder state.

<sup>j</sup> No fluorescence was detectable in the solid state.

state fluorescence quenching was observed for **4a**, **6a** and **4b**. Fluorescence quenching associated with strong intermolecular  $\pi-\pi$  interactions of the similar chromophores has been reported [9].

Spectral data for dyes **8–11** together with the parent dye **7** are summarized in Table 2. Dye **7** absorbs at 458 nm and emits at 538 nm in dimethoxyethane [5]. Extension of the  $\pi$ -system of **7** by condensation with an arylaldehyde produces an increase of the  $\varepsilon_{\max}$  value but has a smaller effect on  $\lambda_{\max}$ . Substituent effects of the aryl moiety (R) are rather small and the mono-azomethine dyes (**8a–11a**) exhibited a hypsochromic shift of  $\lambda_{\max}$ . However, the  $\varepsilon_{\max}$  values increased by between 4.5 to 17 times. Their  $F_{\max}$  values also showed a hypsochromic shift compared with that of **7**, except for **11a** for which a bathochromic shift to 554 nm was observed because of a larger SS value (161 nm) compared with the others (79–110 nm). The  $\lambda_{\max}$  in the solid state (film) exhibited a small hypsochromic shift compared with those in the solution (except **8a**), but the  $F_{\max}$  values generally

showed a large bathochromic shift especially in the cases of **9a** (113 nm) and **10a** (100 nm). Red light emission around 620–640 nm is anticipated for these light emitting materials in EL devices.

On the other hand, bis-azomethine dyes **9b–11b** gave a bathochromic shift of their  $\lambda_{\max}$  and  $F_{\max}$  values, and their  $\varepsilon_{\max}$  values increased in comparison with the corresponding mono-azomethine dyes. Their SS values are almost the same and are in the range 72–82 nm. Comparison of the absorption spectra in solution and vapor deposited thin film of **9b** together with fluorescence spectra in solution are illustrated in Fig. 2. A very broad absorption spectrum from 400 to 600 nm was observed for the thin film which indicated significant aggregation and formation of molecular stacking states. However, its solid state fluorescence spectrum was observed as a single peak at 616 nm (film) and 716 nm (powder). These results indicated that solid state fluorescence was emitted from the lowest energy level of the aggregates.

Table 2

Substituent effects on the absorption and fluorescence spectra of azomethine dyes (**8–11**) in solution and in the solid state

Dye no.	$\lambda_{\max}$ (nm) <sup>a</sup>	$\delta\lambda^b$	$\epsilon_{\max}$	$F_{\max}^a$ (nm)	$\delta F^c$	SS <sup>d</sup> (nm)	$\lambda_{\max}$ (nm) <sup>e</sup>	$\Delta\lambda^f$	$F_{\max}$ (nm) <sup>g</sup>	$\Delta F^h$	R.I. <sup>i</sup>
<b>7</b>	458	–	2600	538	–	80					
<b>8a</b>	414	–44	11,600	493	–45	79	440s	26	543	50	1800
<b>9a</b>	413	–45	44,900	523	–15	110	394	–19	636	113	900
<b>10a</b>	420	–38	44,400	523	–15	103	412	–8	623	100	400
<b>11a</b>	393	–65	38,500	554	16	161	393	0	546	–8	2500
<b>9b</b>	507	49	67,300	589	51	82	573	66	716	127	1900
<b>10b</b>	519	61	80,500	596	58	77	529	10	679	83	3300
<b>11b</b>	473	15	– <sup>j</sup>	545	7	72	530	57	599	54	3300

<sup>a</sup> Measured in chloroform.<sup>b,c</sup> Substituent effects in  $\lambda_{\max}$  and  $F_{\max}$ , respectively.<sup>d</sup> Stokes shift,  $F_{\max} - \lambda_{\max}$  in solution.<sup>e</sup> Measured in the vapor deposited thin film.<sup>f</sup>  $\Delta\lambda = \lambda_{\max}(\text{solid}) - \lambda_{\max}(\text{solution})$ .<sup>g</sup> Measured in the powder state.<sup>h</sup>  $\Delta F = F_{\max}(\text{solid}) - F_{\max}(\text{solution})$ .<sup>i</sup> Relative intensity of fluorescence in the powder state.<sup>j</sup> Not detectable because of low solubility.

In conclusion, symmetrical bis-azomethine dyes **8b–11b** are valuable as new fluorescence chromophores having large  $\epsilon_{\max}$  values (color values) and long wavelength absorption and emission. Indeed, all of the solid state fluorescence was observed in the red light region at 716 nm (**9b**), 679 nm (**10b**) and 599 nm (**11b**). The bis-azomethine dyes (**9b–11b**) have completely planar structures and their intermolecular  $\pi-\pi$  interactions affect their fluorescence quenching in the solid state. The relative strength of fluorescence in the powder state was affected by the substituents but these values did not change so much. The chromophore does not have a dipole moment at the molecular level and molecular stacking behaviour should be revealed by their X-ray crystal analyses. Dye **11b** showed red fluorescence in the solid state and has strong aggregation properties; after purification by silica gel column chromatography using chloroform as eluent, the separated solid is not soluble in any organic solvent and is scarcely vaporized at 420°C in mass spectral measurements indicating strong intermolecular interactions in aggregates. The relationship between solid state fluorescence quenching and molecular stacking with respect to their intermolecular  $\pi-\pi$  interaction will be reported in due course.

### 3. Experimental

#### 3.1. Materials and equipment

The <sup>1</sup>H NMR spectra were measured on a Varian Unity-plus 300 NMR spectrometer for solutions in deuteriochloroform with tetramethylsilane as an internal standard;  $\delta$  values are in ppm and coupling constants values in Hz. Mass spectra were recorded on a Shimadzu GCMS-QP5000 spectrometer. The UV/visible and fluorescence spectra were measured on Hitachi U-2010 and Hitachi F-4500 fluorescence spectrophotometers, respectively. Solid state fluorescence spectra in the powder state (particle size was not controlled) were measured on a Hamamatsu Photonic Multi-channel Analyzer PMA-11 using a Jasco SM-3 type monochromator as a light source. Fluorescent strength in the solid state were determined by using monochromator ( $\pm 10$  nm wavelength range) for excitation, and the emitted fluorescence was quantitatively determined by using a multi-channel analyzer. But the calibration of fluorescent strength depending on the excitation and emission wavelength were not performed. And then, the fluorescent strength in the Tables 1 and 2 were relative values in the range of relatively small

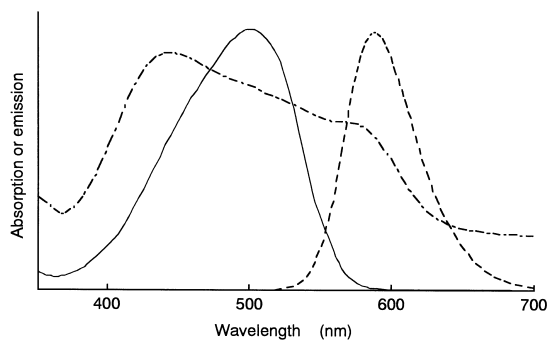


Fig. 2. Absorption spectra in chloroform (507 nm, —), vapor deposited thin film (---), and fluorescence spectra in chloroform (589 nm, .....), of dye **9b**. Its solid state fluorescence was observed at 616 nm in the vapor deposited thin film and at 716 nm in the powder state.

wavelength ranges. We intend to know the big differences in the solid state fluorescence depending on the same chromophoric system. Melting points were determined on a Yamato melting point apparatus (MP-21) without correction. Elemental analyses were conducted with a Yanaco CHN MT-3 recorder. Wako gel C-300 (silica gel) was used for column chromatography.

Diaminomaleonitrile and 2,5-diamino-3,6-dicyano pyrazine were obtained from Nippon Soda Co., Ltd.

### 3.2. General procedure for N-(arylmethylidene)diaminomaleonitriles **2a–6a**

A mixture of diaminomaleonitrile (**1**, 5.0 mmol), arylaldehyde (5.0 mmol), and piperidine (several drops) in benzene was refluxed in a flask equipped with a Dean-Stark trap to remove generated water. After 6 h, the mixture was cooled to room temperature and filtered. The product was isolated by column chromatography on silica gel using chloroform as eluent and was recrystallized from chloroform to give **2a–6a**.

### 3.3. N-[4-Methoxyphenyl)methylidene]diaminomaleonitrile **2a**

From 4-methoxybenzaldehyde as a pale greenish-yellow solid (44%), m.p. 220–221°C;  $\delta_{\text{H}}$  (DMSO- $d_6$ )

8.206 (1H, s, CH=N), 7.987 (2H, d,  $J$  6.3, 2-H, 6-H), 7.756 (2H, broad, NH<sub>2</sub>), 7.023 (2H, d,  $J$  6.3, 3-H, 5-H), 3.840 (3H, s, OMe); C<sub>12</sub>H<sub>10</sub>N<sub>4</sub>O requires C, 63.71; H, 4.46; N, 24.77. Found: C, 63.75; H, 4.48; N, 24.46; M<sup>+</sup> 226. Solid state fluorescence was not detectable.

### 3.4. N-[4-Dimethylaminophenyl)methylidene]diaminomaleonitrile **3a**

From 4-dimethylaminobenzaldehyde as a yellowish-orange solid (35%), m.p. 211–213°C (dec.); C<sub>13</sub>H<sub>13</sub>N<sub>5</sub> requires C, 65.25; H, 5.48; N, 29.27. Found: C, 65.06; H, 5.29; N, 29.03; M<sup>+</sup> 239.  $F_{\text{max}}$  (thin film): 548 nm.

### 3.5. N-[4-Diethylaminophenyl)methylidene]diaminomaleonitrile **4a**

From 4-diethylaminobenzaldehyde as a yellowish-orange solid (52%), m.p. 202–203°C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 8.262 (1H, s, CH=N), 7.668 (2H, d,  $J$  9.0, 2-H, 6-H), 6.664 (2H, d,  $J$  9.0, 3-H, 5-H), 4.891 (2H, s, NH<sub>2</sub>), 3.439 (4H, q,  $J$  7.2, CH<sub>2</sub>), 1.219 (6H, t,  $J$  7.2, Me); C<sub>15</sub>H<sub>17</sub>N<sub>5</sub> requires C, 67.39; H, 6.41; N, 26.20. Found: C, 67.65; H, 6.42; N, 25.66; M<sup>+</sup> 267.  $F_{\text{max}}$  (thin film): 544 nm.

### 3.6. N-[9-Julolidinyl)methylidene]diaminomaleonitrile **6a**

From 9-formyljulolidine as a dark yellow solid (9.6%), m.p. 213–214°C; C<sub>17</sub>H<sub>17</sub>N<sub>5</sub> requires C, 70.08; H, 5.88; N, 24.04. Found: C, 70.22; H, 5.90; N, 23.56; M<sup>+</sup> 291.  $F_{\text{max}}$  (thin film) was not detectable.

### 3.7. General procedure for N,N'-bis(arylmethylidene)diaminomaleonitriles **2b–6b**

A mixture of diaminomaleonitrile (**1**, 5.0 mmol), arylaldehyde (10.0 mmol), and piperidine (several drops) in benzene was refluxed in a flask equipped with a Dean-Stark trap to remove generated water. After 6 h, the mixture was cooled to room temperature and filtered. The product was isolated by column chromatography on silica gel using chloroform as eluent

and was recrystallized from chloroform to give **2b–6b**.

**3.8. N,N'-Bis[(4-methoxyphenyl)methylidene]diaminomaleonitrile 2b**

From 4-methoxybenzaldehyde as a orange solid (69%), m.p. 276–277°C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 8.729 (2H, s, CH=N), 7.973 (4H, d, *J* 8.6, 2-H, 6-H), 7.015 (4H, d, *J* 8.6, 3-H, 5-H), 3.914 (6H, s, OMe); C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>O<sub>2</sub> requires C, 69.75; H, 4.68; N, 16.27. Found: C, 69.55; H, 4.67; N, 16.01; M<sup>+</sup> 344. Solid state fluorescence was not detectable.

**3.9. N,N'-Bis[(4-dimethylaminophenyl)methylidene]diaminomaleonitrile 3b**

From 4-dimethylaminobenzaldehyde as a purple solid (13%), m.p. 279–280°C; C<sub>22</sub>H<sub>22</sub>N<sub>6</sub> requires C, 71.33; H, 5.99; N, 22.69. Found: C, 71.31; H, 5.94; N, 22.43; M<sup>+</sup> 370. *F*<sub>max</sub> (thin film): 624 nm.

**3.10. N,N'-Bis[(4-diethylaminophenyl)methylidene]diaminomaleonitrile 4b**

From 4-diethylaminobenzaldehyde as a dark blue solid (23%), m.p. 234–235°C;  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 9.709 (2H, s, CH=N), 7.718 (4H, d, *J* 9.0, 2-H, 6-H), 6.712 (4H, d, *J* 9.0, 3-H, 5-H), 3.440 (8H, q, *J* 7.2, CH<sub>2</sub>), 1.216 (12H, t, *J* 7.2, Me); C<sub>26</sub>H<sub>30</sub>N<sub>6</sub> requires C, 73.21; H, 7.09; N, 19.70. Found: C, 73.18; H, 7.03; N, 19.10; M<sup>+</sup> 426. *F*<sub>max</sub> (thin film): 622 nm.

**3.11. N,N'-Bis[(9-ethylcarbazol-3-yl)methylidene]diaminomaleonitrile 5b**

From 9-ethyl-3-formylcarbazole as a bright red solid (44%), m.p. > 300°C; C<sub>34</sub>H<sub>26</sub>N<sub>6</sub> requires C, 78.74; H, 5.05; N, 16.21. Found: C, 78.31; H, 5.35; N, 15.96; M<sup>+</sup> 518. *F*<sub>max</sub> (thin film): 577 nm.

**3.12. N,N'-Bis[(9-julolidinyl)methylidene]diaminomaleonitrile 6b**

From 9-formyljulolidine as a dark green solid (23%), m.p. 283–284°C; C<sub>17</sub>H<sub>17</sub>N<sub>5</sub> requires C, 70.08; H, 5.88; N, 24.04. Found: C, 70.22; H, 5.90;

N, 23.56; M<sup>+</sup> 291. Solid state fluorescence was not detectable.

**3.13. General procedure for 2-amino-5-[(aryl)methylidene]amino]-3,6-dicyanopyrazines 8a–11a**

A mixture of 2,5-diamino-3,6-dicyanopyrazine (7, 5.0 mmol) and arylaldehyde (10.0 mmol) in benzene (40 ml) and dimethylacetamide (20 ml) in the presence of diphosphorus pentoxide (0.5 g) was stirred at 80°C. After 4 h the mixture was cooled to room temperature and filtered. The filtrate was evaporated to remove benzene and the residue was quenched with water. The precipitate was collected and purified by column chromatography on silica gel using chloroform as eluent and was recrystallized from chloroform to give **8–11**.

**3.14. 2-Amino-5-[(4-methoxyphenyl)methylidene]amino]-3,6-dicyanopyrazine 8a**

From 4-methoxybenzaldehyde as a dark yellow solid (18%), m.p. 223–225°C (dec.); C<sub>14</sub>H<sub>10</sub>N<sub>6</sub>O requires C, 60.43; H, 3.62; N, 30.20. Found: C, 60.53; H, 3.71; N, 30.03; M<sup>+</sup> 278. *F*<sub>max</sub> (thin film): 507 nm.

**3.15. 2-Amino-5-[(4-dimethylaminophenyl)methylidene]amino]-3,6-dicyanopyrazine 9a**

From 4-dimethylaminobenzaldehyde as a red solid (41%), m.p. 252–254°C (dec.); C<sub>15</sub>H<sub>13</sub>N<sub>7</sub> requires C, 61.84; H, 4.50; N, 33.66. Found: C, 61.65; H, 4.40; N, 33.44; M<sup>+</sup> 291. *F*<sub>max</sub> (thin film): 591 nm.

**3.16. 2-Amino-5-[(4-diethylaminophenyl)methylidene]amino]-3,6-dicyanopyrazine 10a**

From 4-diethylaminobenzaldehyde as a red solid (6.4%), m.p. 196–198°C (dec.);  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 9.008 (1H, s, CH=N), 7.898 (2H, d, *J* 8.1, 2-H, 6-H), 6.702 (2H, d, *J* 8.1, 3-H, 5-H), 5.267 (2H, broad, NH<sub>2</sub>), 3.463 (4H, q, *J* 8.1, CH<sub>2</sub>), 1.246 (6H, t, *J* 8.1, Me); C<sub>17</sub>H<sub>17</sub>N<sub>7</sub> requires C, 63.93; H, 5.37; N, 30.70. Found: C, 63.91; H, 5.28; N, 30.51; M<sup>+</sup> 319. *F*<sub>max</sub> (thin film): 581 nm.



3.17. 2-Amino-5-[[ (9-ethylcarbazol-3-yl) methylidene]amino]-3,6-dicyanopyrazine **11a**

From 9-ethyl-3-formylcarbazole as a yellow solid (32%), m.p. 240–242°C (dec.); C<sub>21</sub>H<sub>15</sub>N<sub>7</sub> requires C, 69.03; H, 4.14; N, 26.83. Found: C, 69.03; H, 4.35; N, 26.54; M<sup>+</sup> 365. F<sub>max</sub> (thin film): 564 nm.

3.18. 2,5-Bis[[ (4-dimethylaminophenyl) methylidene] amino]-3,6-dicyanopyrazine **9b**

From 4-dimethylaminobenzaldehyde as a black solid (14%), m.p. > 300°C; C<sub>24</sub>H<sub>22</sub>N<sub>8</sub> requires C, 68.23; H, 5.25; N, 26.52. Found: C, 68.08; H, 5.12; N, 26.23; M<sup>+</sup> 422. F<sub>max</sub> (thin film): 616 nm.

3.19. 2,5-Bis[[ (4-diethylaminophenyl) methylidene] amino]-3,6-dicyanopyrazine **10b**

From diethylaminobenzaldehyde as a dark purple solid (41%), m.p. 264–265°C; δ<sub>H</sub> (CDCl<sub>3</sub>) 9.146 (2H, s, CH=N), 7.960 (4H, d, J 9.0, 2-H, 6-H), 6.722 (4H, d, J 9.0, 3-H, 5-H), 3.483 (8H, q, J 7.2, CH<sub>2</sub>), 1.252 (12H, t, J 7.2, Me); C<sub>28</sub>H<sub>30</sub>N<sub>8</sub> requires C, 70.27; H, 6.32; N, 23.41. Found: C, 70.46; H, 6.49; N, 23.34; M<sup>+</sup> 478. F<sub>max</sub> (thin film): 630 nm.

3.20. 2,5-Bis[[ (9-ethylcarbazol-3-yl) methylidene] amino]-3,6-dicyanopyrazine **11b**

From 9-ethyl-3-formylcarbazole as a dark orange solid (12%), m.p. > 300°C; C<sub>36</sub>H<sub>26</sub>N<sub>8</sub>

requires C, 75.77; H, 4.59; N, 19.64. Found: C, 75.66; H, 4.92; N, 18.55; M<sup>+</sup> 570. F<sub>max</sub> (thin film): 593 nm.

## References

- [1] Tang CW, Van Slyke SA. Organic electroluminescent diodes. *Appl Phys Lett* 1987;51:913–5.
- [2] Matsuoka M. New syntheses of dicyanopyrazine related functional dyes: functionalities and molecular stacking. *Colour Science* '98 1999;1:99–110.
- [3] Tokita S, Kojima M, Kai N, Kuroki K, Nishi H, Tomoda H et al. Synthesis and properties of 2,3,9,10,16,17,23,24-octaalkyltetrapyrazinoporphyrazines. *Nihon Kagaku Kaishi*, 1990; 219–224 (*Chem. Abstr.*, 1990; 113: 6304a).
- [4] Begland RW, Hartter DR, Jones FN, Sam DJ, Sheppard WA, Webster OW et al. Hydrogen cyanide chemistry. VIII. New chemistry of diaminomaleonitrile. Heterocyclic synthesis. *J Org Chem* 1974;39:2341–50.
- [5] Shirai K, Yanagisawa A, Takahashi H, Fukunishi K, Matsuoka M. Syntheses and fluorescent properties of 2,5-diamino-3,6-dicyanopyrazine dyes. *Dyes and Pigments* 1998;39:49–68.
- [6] Jaung JY, Matsuoka M, Fukunishi K. Syntheses and properties of new styryl dyes derived from 2,3-dicyano-5-methylpyrazines. *Dyes and Pigments* 1996;31:141–53.
- [7] Ohtsuka Y. Chemistry of diaminomaleonitrile. II. Preparation of the open-chain adduct with ketones in diphosphorus pentoxide-ethanol system. *J Org Chem* 1976;41:629–33.
- [8] Begland R W, (Du Pont). Preparation of disperse bisanil dyes derived from diaminomaleonitrile. US patent, 1976; 3962220 (*Chem. Abstr.*, 1976; 85: 79682k).
- [9] Shirai K, Matsuoka M, Fukunishi K. Fluorescence quenching by intermolecular π–π interactions of 2,5-bis(N,N-dialkylamino)-3,6-dicyanopyrazines. *Dyes and Pigments* 1999;42:95–101.