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Syntheses and Fluorescent Properties of 2,5-Diamino-3,6-dicyanopyrazine Dyes

Kazuko Shirai,[a] Atsushi Yanagisawa,[b] Hiroshi Takahashi,[b] Koushi Fukunishi[a] & Masaru Matsuoka[c]*

[a]Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo, Kyoto 606, Japan
[b]Speciality Chemicals Laboratory, Odawara Research Center, Nippon Soda Co., Ltd., Takada, Odawara, Kanagawa 250-02, Japan
[c]Laboratory of Material Science, Kyoto Women's University, Imakumano, Higashiyama, Kyoto 605, Japan

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ABSTRACT

*2,5-Diamino-3,6-dicyanopyrazine (**2**), a new fluorescent chromophore for functional dye materials, was synthesized by an oxidative coupling reaction of 2,3-diamino-3-(phenylthio)acrylonitrile (**1**). Compound **2** has a symmetrical structure and a strong intramolecular charge-transfer chromophoric system. It shows strong yellowish-green fluorescence in solution, and thus has good potential as a synthetic intermediate for fluorescent dye chromophores. Alkylation of the amino groups of **2** produced a bathochromic shift of λ_{max} and resulted in red fluorescence in high quantum yield. On the contrary, acylation of the amino groups produced a hypsochromic shift of λ_{max}, with blue fluorescence in high quantum yield. Modifications of the amino and cyano groups in **2** were studied in detail and many new fluorescent dyes were obtained. The absorption and fluorescent properties, together with fluorescence quantum yield of the substituted amino-3,6-dicyanopyrazines were correlated with their chemical structures.*

Keywords: 2,5-diamino-3,6-dicyanopyrazine, new dye chromophore, pyrazino fluorescent dye, solid state fluorescence, fluorescence quantum yield.

*Corresponding author. Fax: +81 75 531 7175; e-mail: gha14151@niftyserve.or.jp

INTRODUCTION

In recent years the focus of research in dye chemistry has largely changed from involvement in the traditional chemistry of dyes and pigments to investigations of functional dyes for electro-optical applications [1]. Fluorescent dyes are currently of interest in various applications, such as emitters for electroluminescence devices [2], in copy-preventing inks, solar energy collecting materials, fluorescent films for greenhouse, and fluorescent colorants for use in various fields.

It is very important to make use of new raw materials for the development of a new dye chromophores which is almost equivalent to developing new functional dye materials. We intend to use the recently developed 2,5-diamino-3,6-dicyanopyrazine as a new synthetic reagent. It can be synthesized from the oxidative coupling reaction of 2,3-diamino-3-(phenylthio)acrylonitrile, which is a stabilized trimer of hydrogen cyanide. Hydrogen cyanide is produced as a by-product in the commercial production of acrylonitrile. Apart from our own researches [3–6], few pyrazine derivatives have been utilised as dye chromophores [7]. Cyanopyrazine chemistry derived from interactions between diaminomaleonitrile and diiminosuccinonitrile has been extensively studied by du Pont [7].

Pyrazine has two nitrogen atoms at the 1,4-positions of a phenyl ring, and can be anticipated to have many functionalities and reactivities in comparison with benzene analogues. One of the typical characteristics of pyrazine dyes is a strong fluorescence, which is currently of great interest in various application fields. Pyrazine dyes derived from diaminomaleonitrile or 2,3-dichloro-5,6-dicyanopyrazine have a rather small molecular size, but have a strong intramolecular charge–transfer chromophoric system which induces a large dipole moment in the excited state compared with the ground state. They also have fluorescence in solution and some have strong fluorescence even on the solid state.

In this paper, we report the syntheses of fluorescent dyes derived from 2,5-diamino-3,6-dicyanopyrazine; their absorption and fluorescent properties in solution and on solid state are correlated with their chemical structures using the PPP MO method.

RESULTS AND DISCUSSION

Synthesis of 2,5-diamino-3,6-dicyanopyrazine (2)

Compound **2** was synthesized in 75% yield by the oxidative coupling reaction of 2,3-diamino-3-(phenylthio)acrylonitrile (**1**) in benzene in the presence

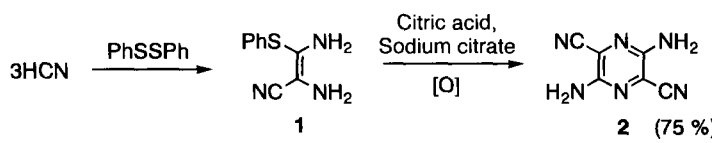
of an aqueous solution of citric acid and sodium citrate under atmospheric oxygen. In the reaction, two equivalents of thiophenol and one equivalent of water were produced, with **2**. Compound **1** was synthesized by the origomerization of three equivalents of hydrogen cyanide in the presence of diphenyldisulfide [8, 9]; it was unstable at room temperature but could be stored in a refrigerator for a month. Diaminomaleonitrile as a tetramer of hydrogen cyanide is known as a useful reagent in the synthesis of pyrazine derivatives [4, 5, 7]. Compound **2** was dark red in appearance and emitted a greenish yellow fluorescence in solution, but did not show any detectable fluorescence in the solid state. It is soluble in dimethylformamide (DMF), dimethylacetamide (DMAC), dimethylsulfoxide (DMSO) and slightly soluble in pyridine, acetone, acetonitrile, ethyl acetate, tetrahydrofuran and 1,2-dimethoxyethane, but insoluble in almost all other organic solvents.

Compound **2** has a symmetrical structure with two amino groups (donor) and two cyano groups (acceptor), and then has an intramolecular charge-transfer chromophoric system evaluated by the PPP MO method. The synthesis of **2** from hydrogen cyanide is shown in Scheme 1. The stereochemistry of **1** was confirmed as a *cis*-diamino structure by NMR and X-ray crystal analysis of the derivative.

Alkylation and cycloalkylation of 2

The two amino groups of **2** have low basicity since they are present on a pyrazine ring having two electron accepting cyano groups. Alkylation of the amino groups of **2** was performed in DMF or DMAC in the presence of strong base. Compound **2** had low solubility because of its molecular symmetry, and introduction of an alkyl group improved its solubility in organic solvents.

Tetramethylation of **2** was examined in various conditions (Table 1), and it was found that the reaction of **2** with methyl iodide in DMAC in the presence of powdered sodium hydroxide at room temperature for 1 h (Run 5) gave the best yields of **3a** in (50–76%). Compound **2** was decomposed by strong bases such as sodium hydroxide or sodium hydride if alkyl halide was not present in the reaction mixture, and the base should be added to the reaction mixture at final stages. Alkyl iodide was found to be the best alkylation reagent compared with other alkyl halides.



Scheme 1

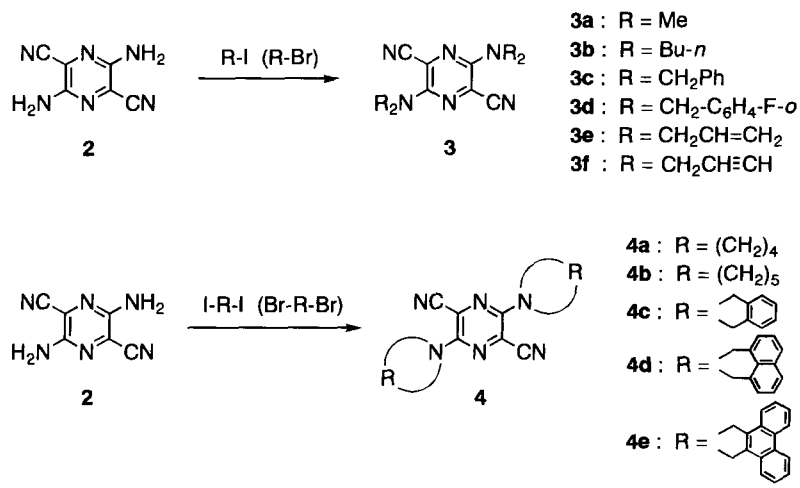
Tetrabutylation of **2** with *n*-butyl iodide in DMAC in the presence of powdered sodium hydroxide at 0°C for 5 h hardly proceeded, and the desired product **3b** was obtained in only 5% yield. On the other hand, tetrabenzylation of **2** with benzyl bromide under similar conditions gave **3c** in 18% yield (Scheme 2). 3-Bromo-1-propene and 3-bromo-1-propyne also gave the 2,5-bis(disubstituted amino)-3,6-dicyanopyrazines (**3e**, **3f**), respectively.

The reactions of **2** with dihalides such as 1,4-diiodobutane, 1,5-diiodopentane, 1,2-bis(bromomethyl)benzene, 1,8-bis(bromomethyl)naphthalene and 9,10-bis(bromomethyl)phenanthrene gave the corresponding 2,5-bis(1-azacycloalkyl-1-yl)-3,6-dicyanopyrazines (**4**). These results were summarized in Table 2.

TABLE 1
Tetramethylation of **2** in Various Conditions[a]

			Reaction conditions			
Run	*Reagent*	*Base*	*Solvent*[b]	*Temp (°C)*	*Time (h)*	*Yield of 3a (%)*
1	$(MeO)_2SO_2$	$NaHCO_3$	$DMSO/H_2O$	60	—	low
2	$(MeO)_3PO$			150	—	12
3	HCHO		HCO_2H	100	5	20
4	MeI	K_2CO_3[c]	DMF	150	5	37
5	MeI	NaOH[c]	DMAC	20	1	50–76

[a]2-Dimethylamino-5-methylamino-3,6-dicyanopyrazine and other products were also obtained as by-products.
[b]DMSO, dimethylsulfoxide; DMF, dimethylformamide; DMAC, dimethylacetamide.
[c]Powder.



Scheme 2

Acylation of 2

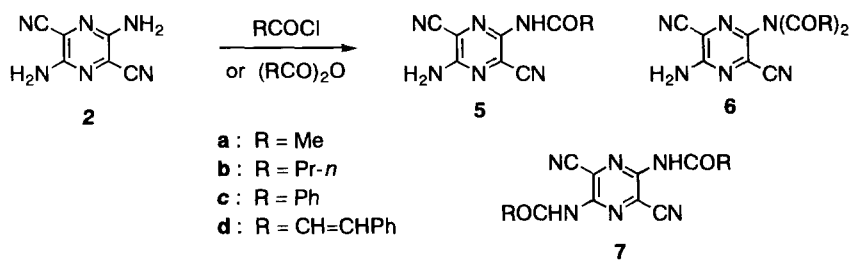
Acylation of the amino groups of **2** was performed by using an acyl chloride and acid anhydride. Reaction of **2** with acetic anhydride under reflux for 8 h gave the N-acetyl **5a**, *N*,*N*-diacetyl **6a** and *N*,*N'*-diacetyl derivatives **7a** in 23, 43, and 6% yields, respectively (Scheme 3). Acetylation of **2** with acetyl chloride in DMAC at room temperature for 10 min gave only the *N*-acetyl derivative **5a** in 90% yield. Similar reaction of **2** with butanoic anhydride at 180°C for 2.5 h gave the corresponding *N*-acyl **5b** and *N*,*N*-diacyl derivatives **6b** in 18 and 60% yields, respectively, but **6b** gradually deacylated to give **5b** under storage.

Reaction of **2** with benzoyl chloride in DMAC gave the *N*-benzoyl derivative **5c** in quantitative yield, but the same reaction in pyridine gave the *N*,*N*-dibenzoyl derivative **6c** in 22% yield. Similar reaction of **2** with cinnamoyl chloride in pyridine gave the corresponding *N*-cinnamoyl **5d** and *N*,*N*-dicinnamoyl derivatives **6d**.

TABLE 2
Tetraalkylation and Cycloamination of **2** in Various Conditions

Run	*Reagent*	*Base*	*Solvent*[a]	*Reaction conditions*		*Product*	*Yield*
				Temp (°C)	*Time (h)*		*(%)*
1	*n*-BuI	NaOH	DMAC	0	5	**3b**	5
2	$PhCH_2Br$	NaH	DMAC	20	0.5	**3c**	18
3	2-F-$C_6H_4CH_2Br$	NaOH	DMAC	0	5	**3d**	50
4	$CH_2=CHCH_2Br$	NaH	DMF	0	2	**3e**	2
5	$CH\equiv CCH_2Br$	NaOH	DMAC	0	2.5	**3f**	10
6	$I(CH_2)_4I$	NaOH	DMAC	20	2	**4a**	57
7	$I(CH_2)_5I$	NaOH	DMAC	20	2	**4b**	38
8	1,2-$(BrCH_2)_2C_6H_4$	NaH	DMF	20	3	**4c**	67
9	1,8-$(BrCH_2)_2C_{10}H_6$	NaH	DMF	0	2	**4d**	63
10	9,10-$(BrCH_2)_2$-phenanthrene	NaH	DMF/CH_2Cl_2	70	24	**4e**	64

[a]DMAC, dimethylacetamide; DMF, dimethylformamide.



Scheme 3

From these results, symmetrical acylation at the 2- and 5-amino groups hardly proceeded, diacylation at the same amino group preferentially occurring. Acylation of **2** produced a hypsochromic shift of absorption and fluorescence spectra, due to the decrease of the donor property of the amino group. Results are summarized in Table 3.

Hydrolysis of 2

Hydrolysis of the cyano group of **2** was carried out stepwise, and direct hydrolysis of the cyano group to the carboxylic acid was unsuccessful.

Hydrolysis of the cyano group of **2** in concentrated sulfuric acid gave 2,5-diamino-3,6-dicarbamoylpyrazine (**9**) in quantitative yield, which was further hydrolyzed by 5% aqueous potassium hydroxide to give 2,5-diamino-3,6-dicarboxypyrazine (**10**) in quantitative yield. Hydrolysis of **2** in aqueous sodium hydroxide gave 2,5-diamino-3-carbamoyl-6-hydroxypyrazine (**8**), together with **9**. In the reaction, one of the cyano groups of **2** was replaced by a hydroxyl group, giving **8**.

Esterification of 10

Esterification of **10** with an alkyl halide in the presence of a strong base such as 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in DMF at room temperature gave the corresponding diester **11**, together with the *N*-alkylated by-products **12** and **13** (Scheme 4).

In the case of ethyl iodide, 2,5-diamino-3,6-bis(ethoxycarbonyl)pyrazine (**11a**), 2-amino-5-ethylamino-3,6-bis(ethoxycarbonyl)pyrazine (**12a**), and 2,5-bis(ethylamino)-3,6-bis(ethoxycarbonyl)pyrazine (**13a**) were obtained in 77, 5

TABLE 3
Acylation of **2** in Various Conditions

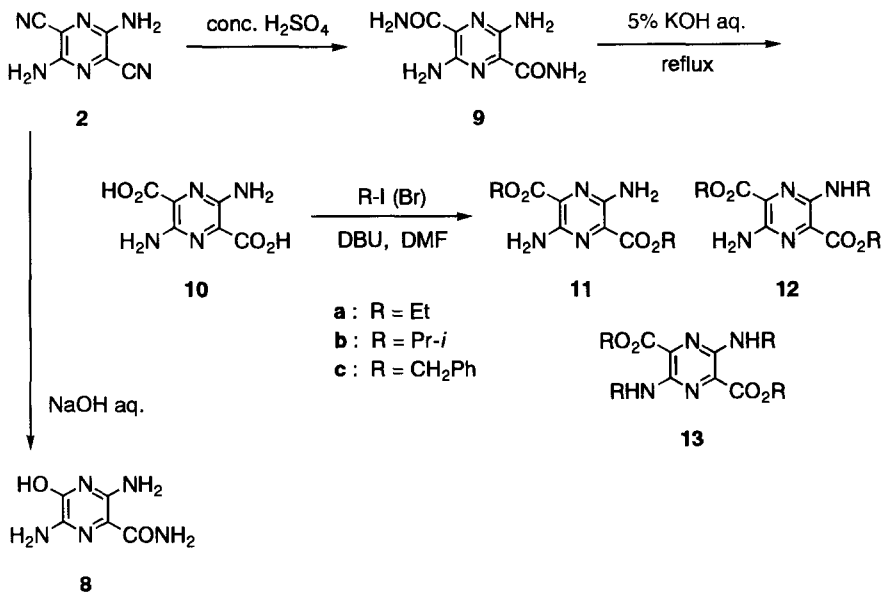
			Reaction conditions			
Run	*Reagent*	*Solvent*[a]	*Temp (°C)*	*Time (h)*	*Product*	*Yield (%)*
1	$(CH_3CO)_2O$		reflux	8	**5a**	23
2	$(CH_3CO)_2O$		reflux	8	**6a**	43
3	$(CH_3CO)_2O$		reflux	8	**7a**	6
4	$(n\text{-}PrCO)_2O$		180	2.5	**5b**	18
5	$(n\text{-}PrCO)_2O$		180	2.5	**6b**	60
6	PhCOCl	DMAC	50	2	**5c**	98
7	PhCOCl	Pyridine	3	0.5	**5b**	42
8	PhCOCl	Pyridine	3	0.5	**6b**	14
9	PhCH=CHCOCl	Pyridine	0	1	**5d**	20
10	PhCH=CHCOCl	Pyridine	0	1	**6d**	40

[a]DMAC: dimethylacetamide.

and 1% yields, respectively. Some results of the esterifications are summarized in Table 4.

Visible and fluorescence spectra

The chromophoric system of **2** was investigated by the PPP MO method, which revealed that **2** has a strong intramolecular charge–transfer character in the first excitation. The calculated results were compared with its benzene analogue, 2,5-diamino-3,6-dicyanobenzene (**14**), which has a similar chromophoric system. From comparison of λ_{max} values, **2** produced a bathochromic shift of 34 nm compared with **14**, due to the electron withdrawing



Scheme 4

TABLE 4
Esterification of **2**

Run	*RX (mol eq)*	*DBU[a] (mol eq)*	*Time (h)*	*Yield (%)*					
				11		*12*		*13*	
1	EtI (7.3)	(7.2)	3.5	**11a**	77	**12a**	5	**13a**	1
2	*i*-PrI (7.2)	(7.2)	2.0	**11b**	30	**12b**	1	**13b**	trace
3	$PhCH_2Br$ (7.2)	(7.2)	4.0	**11c**	58	**12c**	5	**13c**	none

[a]1,8-Diazabicyclo[5.4.0]-7-undecene.

ability of the ring nitrogens. The frontier energy levels (ε_{HOMO}, ε_{LUMO}) and the first excitation energy (ΔE_1), π-electron density changes accompanying the first excitation are summarized in Fig. 1.

The calculated λ_{max} of **2** and **14** were well in accordance with the observed values, but the calculated oscillator strength of **2** was much larger than that of **14**, which are the reverse values of those observed (Scheme 5).

The bathochromic shift of **2** was explained by the difference between the energy levels of the frontier orbitals and, the relatively much lower ε_{LUMO} value of **2** indicates much the stronger electron withdrawing ability of **2** compared with **14**. The π-electron density changes of **2** also indicate the acceptor ability of the ring-nitrogen (increase of electron densities at these nitrogens). From these calculated results for the chromophoric system, the following substituent effects are proposed: *N*-alkylation produces a bathochromic shift of λ_{max}, but acylation of the amino groups produces a hypsochromic shift. Hydrolysis of the cyano groups also produces a hypsochromic shift. These conclusions are well evidenced in the observed results summarized in Table 5.

Pyrazine derivatives have strong fluorescence, and the fluorescence maximum (F_{max}) in solution and solid state are summarized in Table 5. They generally have quite large Stokes' shift of 70–100 nm, but some have shifts

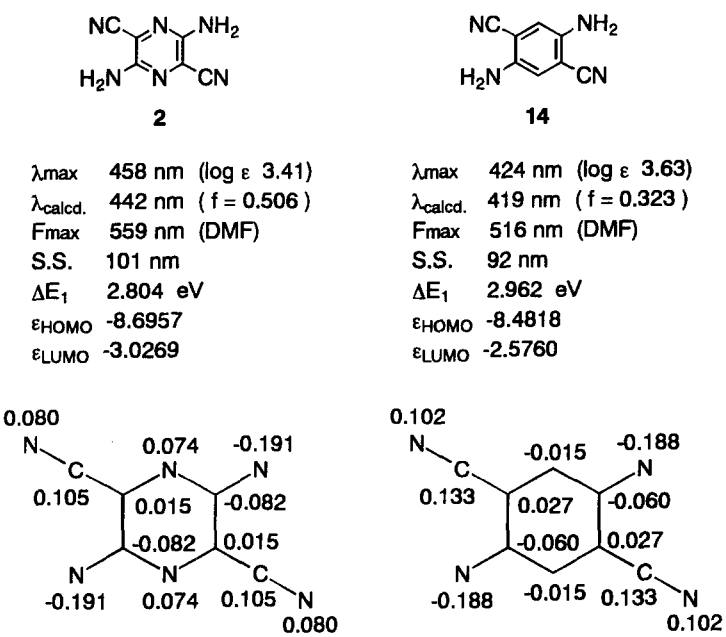
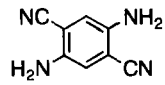


Fig. 1. Comparison of absorption and fluorescence spectra and their calculated results by PPP MO method.



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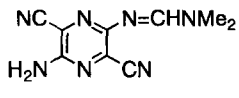

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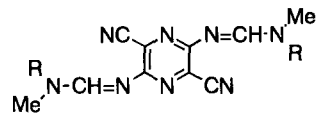
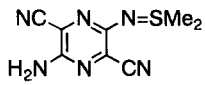


16a R = Me
16b R = Ph



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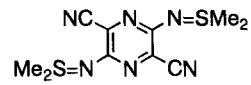

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Scheme 5

over 100 nm. The ΔF value indicates the difference of F_{max} from solid state to solution, which indicates the effect of molecular stacking on the fluorescent spectra. This was affected largely by the substituent at the amino groups, and **4a** (105 nm), **11a** (100 nm) and **12a** (80 nm) showed large values, indicating much stabilization of the excited state in the solid state. Fluorescence in the solid state is very important for fluorescent functional materials and colorants, and these large Stokes' shift, together with a bathochromic shift of F_{max} in the solid state, indicate that those compounds can be used as interesting fluorescent materials; for example dye **4a** is orange in color but shows red fluorescence in the solid state; dye **11a** is yellow but shows a red fluorescence and dye **5d** is pale yellow but shows an orange fluorescence. These large differences in color, including fluorescence, further indicate their potential use as coloring matters which can be utilised as functional dye materials in various practical uses. Substituent effects on their solid state fluorescence are not fully clear, but some of steric requirements in the molecular stacking of these dyes needs to be considered.

The fluorescence quantum yield (relative values) of some dyes were measured, as shown in Table 5. Dye **2** has quite a high fluorescence quantum yield of 0.3, which was increased to 0.4 by tetramethylation (**3a**). The *N*,*N*-dibenzoyl derivative **6c** showed the highest yield of 0.8, and the azomethine dye **15** also showed the value of 0.8. However, the sulfur analogue (**18**) of dye **15** showed only weak fluorescence. Substituent effects on the fluorescence quantum yield of pyrazine dyes will be studied in more detail and the results reported in due course.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Joel FX 270 (270 MHz) spectrometer, IR spectra on a Perkin–Elmer 1760X and on Mass spectra on Hitachi M-80 and Shimadzu GCMS-QP5000 spectrometers. UV/visible and fluorescence spectra were measured on a Shimadzu PR-1 spectrophotometer and a Hitachi 850 fluorescence spectrophotometer, respectively. Melting points were determined on a Shimadzu DSC-50 and a MRK Melt Pointer

TABLE 5
Absorption and Fluorescence Spectra of Compounds **2–18**

Compd. no.	λ_{max} *(log ε) (nm)*	F_{max} *(soln.) (nm)*	F_{max} *(solid) (nm)*	*SS*[a] *(nm)*	*ΔF (nm)*	*Quantum yield (Φ)*
2	458 (3.41)[b]	538[b]	—[h]	80	—	0.3
3a	495 (3.64)[b]	594[b]	643	99	49	0.4
3b	522 (3.68)[c]	603[c]	651	81	48	—
3c	484 (3.27)[b]	574[b]	576	90	2	—
3d	478 (3.66)[c]	565[c]	—	87	—	—
3e	488 (3.51)[b]	571[b]	—	83	—	—
3f	446 (3.68)[c]	532[c]	547	86	15	—
4a	526 (3.74)[c]	601[c]	706	75	105	0.3
4b	492 (3.59)[c]	607[c]	629	115	22	—
4c	506 (3.51)[b]	582[b]	—	76	—	—
4d	477 (3.67)[d]	581[d]	582	104	1	—
5a	396 (3.78)[b]	485[b]	—	89	—	—
6a	387 (3.78)[b]	455[b]	—	68	—	—
7a	357 (3.84)[b]	432[b]	—	75	—	—
5c	403 (3.71)[e]	488[e]	483	85	−5	—
6c	402 (3.76)[e]	488[e]	484	86	−4	0.8
5d	390 (3.67)[c]	468[c]	544	78	76	—
6d	378 (3.94)[c]	452[c]	469	74	17	—
10	406 (3.57)[f]	536[f]	—[h]	130	—	—
11a	458 (3.88)[c]	544[c]	644	86	100	—
11b	454 (3.85)[c]	545[c]	602	91	57	—
12a	488 (3.82)[c]	572[c]	652	84	80	—
14	424 (3.63)[e]	516[e]	524	92	8	—
15	452 (3.84)[c]	527[c]	590	75	63	0.8
16a	456 (3.91)[c]	525[c]	617	69	92	—
16b	440 (3.96)[g]	532[g]	—	92	—	—
17	513 (3.74)[e]	613[e]	—[h]	100	—	—
18	526 (3.61)[e]	651[e]	699	125	48	< 0.1

[a]Stokes' shift.
[b]Measured in 1,2-dimethoxyethane.
[c]In chloroform.
[d]In dichloromethane.
[e]In dimethylformamide.
[f]In water.
[g]In acetonitrile.
[h]Not detectable.

(Prism Scope Type) apparatus without correction. Elemental analyses were conducted with a Yanaco CHN MT-3 recorder. Wako gel C-200 (silica gel) was used for column chromatography.

2,5-Diamino-3,6-dicyanopyrazine (2)

To 2,3-diamino-3-(phenylthio)acrylonitrile (**1**, 6.15 g, 32 mmol) in benzene (76 ml) and water (245 ml) were added 0.1 M citric acid (320 ml) and 0.1 M sodium citrate (26 ml) to make the solution pH 3 at room temperature. After stirring with bubbling of air for 4 h at 20°C, the separated red powder was isolated by filtration, washed with water (100 ml) and *n*-hexane/ethyl acetate (v/v = 1/1, 150 ml), and dried at 40°C for 4 h to give **2**. Yield 1.93 g (75%), m.p. > 280°C. ^{13}C NMR (DMSO-d_6): δ 113.3 (s), 115.1 (s), 149.7 (s) ppm. IR (KBr): 3399, 3319, 3205, 2233, 1639, 1487, 1412, 1230, 1203 cm^{-1}. UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 266 (4.48) and 458 (3.41) nm. Fluorescent spectrum, F_{max}: (1,2-dimethoxyethane) 538 nm. Fluorescence quantum yield (Φ) 0.3.

Many compounds can be used as an acid catalyst and an oxidant in synthesis of **2**, and the yield of **2** using these varied from 45 to 82%.

2,5-Bis(dimethylamino)-3,6-dicyanopyrazine (3a) (alkylation of 2, general procedure)

2,5-Diamino-3,6-dicyanopyrazine (**2**, 2.0 mmol) and methyl iodide (33.7 mmol) were dissolved in distilled dimethylacetamide (10 ml) cooled with ice, and powdered sodium hydroxide (0.48 g) was added gradually with stirring. After stirring at room temperature for 1 h, distilled water (100 ml) and dichloromethane (50 ml) were added to the reaction mixture. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The product was isolated by column chromatography on silica gel using benzene as the eluent and recrystallized from benzene/*n*-hexane (v/v = 1/1) to give **3a**. Yield 76%, m.p. 123.4–124.5°C. ^{13}C NMR ($CDCl_3$): δ 40.2 (q), 112.8 (s), 116.5 (s), 150.7 (s) ppm. ^{1}H NMR ($CDCl_3$): δ 3.17 (12H, s, CH_3) ppm. IR (KBr): 2945, 2884, 2215, 1538, 1404, 1230 cm^{-1}. Mass (*m/z*): 216 (M^+). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 297 (4.35) and 495 (3.64) nm. F_{max}: (1,2-dimethoxyethane) 594, (solid) 643 nm. Fluorescence quantum yield (Φ) 0.4.

Anal. Calcd. for $C_{10}H_{12}N_6$: C, 55.54; H, 5.59; N, 38.87%. Found: C, 55.82; H, 5.52; N, 38.94%.

Other **3** and **4** were similarly prepared:

2,5-Bis(di-*n*-butylamino)-3,6-dicyanopyrazine (*3b*)

Yield 5%, as oil. ^{13}C NMR ($CDCl_3$): δ 13.9 (q), 20.0 (t), 30.1 (t), 50.1 (t), 112.9 (s), 116.7 (s), 149.0 (s) ppm. ^{1} NMR ($CDCl_3$): δ 0.95 (12H, t, $J=7.4$, CH_3), 1.35 (8H, sextet, $J=7.4$, $CH_2CH_2CH_3$), 1.59 (8H, tt, $J=7.8$, 7.4, $CH_2CH_2CH_2$), 3.48 (8H, t, $J=7.8$, NCH_2CH_2) ppm. Mass (*m/z*): 384 (M^+). UV-Vis ($CHCl_3$) λ_{max} (log ε): 305 (4.42) and 522 (3.68) nm. F_{max}: ($CHCl_3$) 603, (solid) 651 nm.

2,5-Bis[bis(benzyl)amino]-3,6-dicyanopyrazine (3c)

Yield 18%, m.p. 105.3°C. ^1H NMR ($CDCl_3$): δ 4.75 (8H, s, CH_2), 7.20 (20H, m, phenyl protons) ppm. IR (KBr): 3030, 2924, 2222, 1499, 1451, 1217 cm^{-1}. Mass (*m/z*): 520 (M^+, 100%). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 301 (4.14) and 484 nm (3.27). F_{max}: (1,2-dimethoxyethane) 574, (solid) 576 nm.

Anal. Calcd. for $C_{34}H_{28}N_6$: C, 78.44; H, 5.42; N, 16.14%. Found: C, 77.80; H, 5.53; N, 15.32%.

2,5-Bis[bis(2-fluorophenylmethyl)amino]-3,6-dicyanopyrazine (3d)

Yield 50%, m.p. 150–151°C. ^{13}C NMR ($CDCl_3$): δ 47.7 (t), 115.5 (d), 115.6 (s), 115.8 (d), 123.3 (s), 123.6 (s), 124.2 (s), 129.5 (d), 129.7 (s), 130.1 (d) ppm. ^1H NMR ($CDCl_3$): δ 4.79 (8H, s, CH_2), 7.04 (4H, dt, phenyl protons), 7.11 (4H, dt, phenyl protons), 7.28 (8H, m, phenyl protons) ppm. IR (KBr): 3066, 2940, 2216, 1619, 1586, 1515, 1487, 1449, 1363, 1222 cm^{-1}. Mass (*m/z*): 592 (M^+). UV-Vis ($CHCl_3$) λ_{max} (log ε): 301 (4.43) and 478 (3.66) nm. F_{max}: ($CHCl_3$) 565 nm.

2,5-Bis[bis(2-propenyl)amino]-3,6-dicyanopyrazine (3e)

Yield 2%, as oil. ^{13}C NMR ($CDCl_3$): δ 51.7 (t), 113.6 (s), 116.2 (s), 118.4 (t), 132.8 (d), 149.4 (s) ppm. ^1H NMR ($CDCl_3$): δ 4.13 (8H, d, $J=5.9$, CH_2), 5.23 (4H, dd, $J=1.1$, 18.1, $=CH_2$), 5.25 (4H, dd, $J=1.1$, 9.2, $=CH_2$), 5.87 (4H, m, $=CH-$) ppm. IR (KBr): 3082, 2984, 2924, 2862, 2221, 1643, 1503, 1417, 1218 cm^{-1}. Mass (*m/z*): 320 (M^+). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 488 (3.51) nm. F_{max}: (1,2-dimethoxyethane) 571 nm.

2,5-Bis[bis(2-propynyl)amino]-3,6-dicyanopyrazine (3f)

Yield 10%, m.p. 113.5–114.5°C. ^{13}C NMR ($CDCl_3$): δ 39.3 (t), 74.1 (d), 115.0 (s), 116.4 (s), 149.7 (s) ppm. ^1H NMR ($CDCl_3$): δ 2.34 (4H, t, $J=2.4$,

≡CH), 4.46 (8H, d, $J=2.4$, CH_2) ppm. IR (KBr): 3276, 2938, 2893, 2237, 2110, 1451, 1423, 1211 cm^{-1}. Mass (*m/z*): 312 (M^+). UV-Vis ($CHCl_3$) λ_{max} (log ε): 298 (4.34) and 446 (3.68) nm. F_{max}: ($CHCl_3$) 532, (solid) 547 nm.

Anal. Calcd. for $C_{18}H_{12}N_6$: C, 69.22; H, 3.87; N, 26.91%. Found: C, 69.31; H, 4.02; N, 26.91%.

2,5-Bis(pyrrolidinyl)-3,6-dicyanopyrazine (4a)

Yield 57%, m.p. 197–198°C. ^{13}C NMR ($CDCl_3$): δ 25.6 (t), 48.8 (t), 112.0 (s), 117.1 (s), 147.7 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.99 (8H, tt, $J=6.8$, 6.8, NCH_2CH_2), 3.63 (8H, t, $J=6.8$, NCH_2CH_2) ppm. IR (KBr): 2969, 2877, 2219, 1501, 1457, 1224 cm^{-1}. Mass (*m/z*): 268 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 301 (4.41) and 526 (3.74) nm. F_{max}: ($CHCl_3$) 601, (solid) 706 nm. Fluorescence quantum yield (Φ) 0.3.

Anal. Calcd. for $C_{14}H_{16}N_6$: C, 62.67; H, 6.01; N, 31.32%. Found: C, 62.81; H, 5.90; N, 31.15%.

2,5-Bis(piperidino)-3,6-dicyanopyrazine (4b)

Yield 38%, m.p. 116.5–117.5°C. ^{13}C NMR ($CDCl_3$): δ 24.2 (t), 25.6 (t), 49.5 (t), 115.9 (s), 116.0 (s), 151.9 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.68 (12H, m, $NCH_2CH_2CH_2$), 3.50 (8H, m, NCH_2CH_2) ppm. IR (KBr): 2948, 2842, 2221, 1478, 1463, 1446, 1259, 1213 cm^{-1}. Mass (*m/z*): 296 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 305 (4.38) and 492 (3.59) nm. F_{max}: ($CHCl_3$) 607, (solid) 629 nm.

Anal. Calcd. for $C_{16}H_{20}N_6$: C, 64.84; H, 6.80; N, 28.36%. Found: C, 64.56; H, 6.91; N, 28.04%.

2,5-Bis(isoindolin-2-yl)-3,6-dicyanopyrazine (4c)

Yield 67%, m.p. 317.6°C. IR (KBr): 3434, 3044, 2896, 2856, 2221, 1490, 1458, 1224 cm^{-1}. Mass (*m/z*): 364 (M^+, 100%). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 302 (4.33), and 506 (3.51) nm. F_{max}: (1,2-dimethoxyethane) 582 nm.

2,5-Bis(1,2,3-trihydro-2-azaphenalen-2-yl)-3,6-dicyanopyrazine (4d)

Yield 63%, m.p. 305°C. IR (KBr): 3436, 3044, 2958, 2232, 1469, 1446, 1265 cm^{-1}. Mass (*m/z*): 464 (M^+, 100%). UV-Vis (CH_2Cl_2) λ_{max} (log ε): 303 (4.70) and 477 (3.67) nm. F_{max}: (CH_2Cl_2) 581, (solid) 582 nm.

Anal. Calcd. for $C_{30}H_{20}N_6$: C, 77.57; H, 4.34; N, 18.09%. Found: C, 77.83; H, 4.52; N, 17.83%.

2,5-Bis(phenanthrene[9,10-c]pyrrolidin-2-yl)-3,6-dicyanopyrazine (4e)

Yield 64%, m.p. 364°C. IR (KBr): 3061, 2854, 2223, 1224 cm^{-1}. Mass: (*m/z*) 564 (M^+, 100%). UV-Vis (CH_2Cl_2) λ_{max}: 297 nm. F_{max}: (CH_2Cl_2) 558 nm.

Anal. Calcd. for $C_{38}H_{24}N_6$: C, 80.83; H, 4.28; N, 14.88%. Found: C, 78.61; H, 4.48; N, 13.92%.

2-Amino-5-acetylamino-3,6-dicyanopyrazine (5a) (acetylation of 2, general procedure)

Compound (**2**, 9 mmol) in acetic anhydride (30 ml) was stirred for 8 h under reflux. After quenching into ice water, the product was filtered and dried. The product mixtures were chromatographed on silica gel using benzene/ethyl acetate (v/v = 1/1) as eluent to give **6a**, **5a** and **7a**, respectively.

2-Amino-5-acetylamino-3,6-dicyanopyrazine (5a)

Yield 23%. ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ 22.7 (q), 112.9 (s), 114.1 (s), 127.5 (s), 138.8 (s), 154.0 (s), 169.4 (s) ppm. ^1H NMR ($CDCl_3$): δ 1.16 (3H, s, CH_3), 4.06 (2H, s, NH_2), 5.70 (1H, s, NH) ppm. IR (KBr): 3384, 3236, 2240, 1686, 1651, 1474, 1388, 1219 cm^{-1}. Mass (*m/z*): 202 (M^+, 100%). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 396 (3.78) nm. F_{max}: (1,2-dimethoxyethane) 485 nm.

2-Amino-5-diacetylamino-3,6-dicyanopyrazine (6a)

Yield 43%. ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ 26.0 (q), 113.1 (s), 113.6 (s), 114.2 (s), 131.2 (s), 138.6 (s), 155.6 (s), 171.5 (s) ppm. ^1H NMR ($CDCl_3$): δ 2.33 (6H, s, CH_3), 7.62 (2H, broad, NH_2) ppm. IR (KBr): 3442, 3335, 2234, 1726, 1631, 1467, 1403, 1228 cm^{-1}. Mass (*m/z*): 244 (M^+). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 387 (3.78) nm. F_{max}: (1,2-dimethoxyethane) 455 nm.

2,5-Bis(acetylamino)-3,6-dicyanopyrazine (7a)

Yield 6%. ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ 23.2 (q), 113.6 (s), 124.1 (s), 145.1 (s), 169.4 (s) ppm. ^1H NMR ($CDCl_3$): δ 2.33 (6H, s, CH_3), 7.62 (2H, broad, NH) ppm. IR (KBr): 3395, 3253, 2237, 1695, 1527, 1427, 1364, 1265 cm^{-1}. Mass (*m/z*): 244 (M^+, 100%). UV-Vis (1,2-dimethoxyethane) λ_{max} (log ε): 357 (3.84) nm. F_{max}: (1,2-dimethoxyethane) 432 nm.

2-Amino-5-benzoylamino-3,6-dicyanopyrazine (5c) and 2-Amino-5-dibenzoylamino-3,6-dicyanopyrazine (6c)

Compound (**2**, 40.0 mmol) was dissolved in pyridine (120 ml) and benzoyl chloride (80.0 mmol) was added dropwise into the solution with stirring at 0°C. After stirring for 30 min, methanol (20 ml) was added and the product was filtered. Water (150 ml) and ethyl acetate (150 ml) were added to the filtrate, and the organic layer was isolated, left overnight and the resulting precipitate filtered, washed with ethyl acetate, and dried to give **5c** in 42% yield. The filtrate was concentrated and column chromatographed on silica gel using benzene/ethyl acetate (v/v = 5/1) as eluent gave **6c** in 14% yield.

5c was also quantitatively synthesized by the following method: Compound (**2**, 10.0 mmol) was dissolved in dimethylacetamide (10 ml) and benzoyl chloride (11.1 mmol) was added with stirred for 2 h at 50°C. After quenching into ice water, the product was filtered, washed with ethyl acetate and dried to give **5c** in 98% yield.

2-Amino-5-benzoylamino-3,6-dicyanopyrazine (5c)

Yield 98%, m.p. 265.5°C. ^{13}C NMR ($CDCl_3$/DMSO-d_6): δ 112.9 (s), 114.2 (s), 128.1 (d), 128.2 (s), 128.3 (d), 132.3 (s), 132.5 (d), 138.5 (s), 154.3 (s), 166.3 (s) ppm. ^1H NMR ($CDCl_3$/DMSO-d_6): δ 7.47 (2H, broad, NH_2), 7.6 (3H, m, phenyl protons), 8.0 (2H, m, phenyl protons), 10.9 (1H, s, NH) ppm. IR (KBr): 3414, 3340, 3245, 2241, 1669, 1469, 1387, 1216 cm^{-1}. Mass (*m/z*): 264 (M^+, 100%). UV-Vis (DMF) λ_{max} (log ε): 340 (3.55) and 403 (3.71) nm. F_{max}: (DMF) 488, (solid) 483 nm.

Anal. Calcd. for $C_{13}H_8N_6$: C, 59.09; H, 3.05; N, 31.81%. Found: C, 60.16; H, 3.43; N, 29.67%.

2-Amino-5-dibenzoylamino-3,6-dicyanopyrazine (6c)

Yield 14%, m.p. 100–101°C. UV-Vis (DMF) λ_{max} (log ε): 275 (4.31) and 402 (3.76) nm. F_{max}: (DMF) 488, (solid) 484 nm. Fluorescence quantum yield (Φ) 0.8.

2-Amino-5-[(3-phenyl-2-propenoyl)amino]-3,6-dicyanopyrazine (5d) and 2-amino-5-[bis(3-phenyl-2-propenoyl)amino]-3,6-dicyanopyrazine (6d)

Compound (**2**, 4.0 mmol) was dissolved in pyridine (30 ml) and cinnamoyl chloride (8.0 mmol) was added with stirring at 0°C. After stirring for 1 h, the mixture of methanol (5 ml), water (60 ml) and ethyl acetate (60 ml) was added into the solution, and the resulting organic layer separated and column

chromatographed on silica gel using benzene/ethyl acetate (v/v = 5/1) as the eluent. The products were recrystallized from dichloromethane and dichloromethane/*n*-hexane to give **5d** and **6d**, respectively.

2-Amino-5-(3-phenyl-2-propenoyl)amino-3,6-dicyanopyrazine (5d)

Yield 20%, m.p. 257°C. ^{13}C NMR (DMSO-d_6): δ 112.8 (s), 114.4 (s), 119.8 (d), 127.1 (s), 127.9 (d), 128.9 (d), 130.2 (d), 134.2 (s), 138.2 (s), 142.2 (d), 153.9 (s), 164.2 (s) ppm. ^1H NMR (DMSO-d_6): δ 6.85 (^1H, d, J = 15.9, =CH–), 7.47 (3H, m, phenyl protons), 7.66 (2H, m, phenyl protons), 7.70 (1H, d, J = 15.9, =CH–). 7.85 (2H, broad, NH_2), 10.93 (1H, s, NH) ppm. IR (KBr): 3411, 3339, 3245, 2242, 1635, 1469, 1387, 1214 cm^{-1}. Mass: (*m/z*) 290 (M^+). UV-Vis ($CHCl_3$) λ_{max} (log ε): 390 (3.67) nm. F_{max}: ($CHCl_3$) 468, (solid) 544 nm.

Anal. Calcd. for $C_{15}H_{10}N_6O$: C, 62.06; H, 3.47; N, 28.95%. Found: C, 62.69; H, 3.65; N, 26.83 %.

2-amino-5-[bis(3-phenyl-2-propenoyl)amino]-3,6-dicyanopyrazine (6d)

Yield 40%, m.p. 196-198°C. ^{13}C NMR ($CDCl_3$): δ 112.9 (s), 113.0 (s), 115.1 (s), 118.8 (d), 128.7 (d), 129.0 (d), 131.2 (d), 131.6 (s), 134.0 (s), 141.3 (s), 147.5 (d), 154.4 (s), 167.5 (s) ppm. ^1H NMR ($CDCl_3$): δ 5.83 (2H, s, NH_2), 6.80 (2H, d, J = 15.4, =CH–), 7.40 (6H, m, phenyl protons), 7.53 (4H, m, phenyl protons), 7.91 (2H, d, J = 15.4, =CH–) ppm. IR (KBr): 3344, 3226, 3061, 2235, 1695, 1619, 1554, 1470, 1328, 1228 cm^{-1}. Mass (*m/z*): 420 (M^+). UV-Vis ($CHCl_3$) λ_{max} (log ε): 378 (3.94) nm. F_{max}: ($CHCl_3$) 452, (solid) 469 nm.

Anal. Calcd. for $C_{24}H_{16}N_6O_2$: C, 68.56; H, 3.84; N, 19.99%. Found: C, 68.27; H, 3.93; N, 19.72%.

2,5-Diamino-3,6-dicarboxypyrazine (10)

Compound (**2**, 50.0 mmol) was dissolved in conc. sulfuric acid (50 ml) and stirred at room temperature for 3 h. The reaction mixture was quenched with water. The separated product was filtered, washed with water and acetone, and dried *in vacuo* to give 2,5-diamino-3,6-dicarbamoylpyrazine (**9**) quantitatively. Compound (**9**, 40.8 mmol) was dissolved in aqueous 5% potassium hydroxide (150 ml) with stirring and the solution heated under reflux for 3 h. After cooling, the solution was acidified with hydrochloric acid, and the product collected by filtration, washed with distilled water and methanol, and then dried *in vacuo* to give **10**. Yield 96%, m.p. 237°C. ^{13}C NMR (DMSO-d_6): δ 125.7 (s), 147.8 (s), 167.1 (s) ppm. ^1H NMR (DMSO-d_6): δ 8.55

(6H, broad, NH_3^+) ppm. IR (KBr): 3446, 3403, 3292, 3018, 1614, 1513, 1459, 1226, 1175 cm$^{minus;1}$. Mass (*m/z*): 198 (M^+, 100%). UV-Vis (H_2O) λ_{max} (log ε): 262 (3.95) and 406 (3.57) nm. F_{max}: (H_2O) 536 nm.

Anal. Calcd. for $C_6H_6N_4O_4 \cdot 1/2H_2O$: C, 34.78; H, 3.38; N, 27.05%. Found: C, 32.58; H, 3.30; N, 27.31%.

2,5-Diamino-3,6-bis(ethoxycarbonyl)pyrazine (11a) and 2-amino-5-ethylamino-3,6-bis(ethoxycarbonyl)pyrazine (12a)

Compound (**10**, 1.5 mmol) was reacted with ethyl iodide (10.9 mmol) in dimethylformamide (5 ml) in the presence of 1,8-diazabicyclo[5.4.0]-7-undecene (1.62 ml) with stirring at room temperature for 3.5 h. The reaction mixture was quenched into water and ethyl acetate, and the product filtered, washed with water and ethyl acetate, and dried to give **11a**. The filtrate was separated into organic and an aqueous layers, and the organic layer was concentrated and column chromatographed on silica gel using benzene/ethyl acetate (v/v = 5/1) as eluent to give **11a**, **12a**, and **13a**.

2,5-Diamino-3,6-bis(ethoxycarbonyl)pyrazine (11a)

Yield 77%, m.p. (decomp.) 231–233°C. ^{13}C NMR (DMSO-d_6): δ 14.1 (q), 61.1 (t), 125.1 (s), 147.8 (s), 165.3 (s) ppm. ^1H NMR (DMSO-d_6): δ 1.31 (6H, t, J = 7.1, CH_3), 4.32 (4H, q, J = 7.1, CH_2), 6.55 (4H, broad, NH_2) ppm. IR (KBr): 3468, 3311, 2986, 1696, 1594, 1420, 1171 cm^{-1}. Mass: (*m/z*) 254 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 458 (3.88) nm. F_{max}: ($CHCl_3$) 544, (solid) 644 nm.

Anal. Calcd. for $C_{10}H_{14}N_4O_4$: C, 47.24; H, 5.55; N, 22.04%. Found: C, 46.89; H, 5.41; N, 21.91%.

2,5-Diamino-3,6-Bis(i-propoxycarbonyl)pyrazine (11b)

Yield 30%, m.p. 233°C. ^1H NMR (DMSO-d_6): δ 1.32 (12H, d, CH_3), 5.17 (2H, septet, CH), 6.40 (4H, s, NH_2) ppm. IR (KBr): 3469, 3310, 2985, 1690, 1592, 1420, 1316, 1187, 1143, 1102 cm^{-1}. Mass (*m/z*): 282 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 454 (3.85) nm. F_{max}: ($CHCl_3$) 545, (solid) 602 nm.

Anal. Calcd. for $C_{12}H_{18}N_4O_4$: C, 51.05; H, 6.43; N, 19.85%. Found: C, 51.20; H, 6.42; N, 19.41%.

2-Amino-5-ethylamino-3,6-bis(ethoxycarbonyl)pyrazine (12a)

Yield 5%, m.p. 142–143°C. ^1H NMR ($CDCl_3$): δ 1.27 (3H, t, J = 7.0, $NHCH_2CH_3$), 1.43 (6H, t, J = 7.2, $CO_2CH_2CH_3$), 3.51 (2H, quin,

$NHCH_2CH_3$), 4.43 (4H, m, $J=7.2$, $CO_2CH_2CH_3$), 5.78 (2H, broad, NH_2), 7.19 (1H, broad, NH) ppm. IR (KBr): 3469, 3381, 3326, 2978, 2936, 2874, 1693, 1614, 1571, 1487, 1324, 1174, 1132 cm^{-1}. Mass (*m/z*): 282 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 488 (3.82) nm. F_{max}: ($CHCl_3$) 572, (solid) 652 nm.

Anal. Calcd. for $C_{12}H_{18}N_4O_4$: C, 51.05; H, 6.43; N, 19.85%. Found: C, 50.41; H, 6.17; N, 19.39%.

1,4-Diamino-2,5-dicyanobenzene (14)

Intermolecular condensation of ethyl 4-chloroacetoacetate (1.46 mol) in the mixture of *iso*-propanol (1 l) and water (780 ml) in the presence of sodium carbonate (62 g) and sodium hydroxide (48 g) gave diethyl 2,5-dihydroxy-1,4-cyclohexadiene-1,4-dicarboxylate in 59% yield. This was then aminated with ammonium acetate at 150°C, followed by aromatization with bromine in chloroform, to give diethyl 1,4-diaminobenzene-2,5-dicarboxylate. The ethyl esters were hydrolyzed with aqueous sodium hydroxide to give 1,4-diamino-benzene-2,5-dicarboxylic acid in 95% yield. The tosylamino derivative was chlorinated with phosphorus pentachloride in benzene and converted into carboxamides with ammonia gas. The tosylamino groups were hydrolyzed into amino groups with concentrated sulfuric acid and the carboxamides were treated with hexaethylphosphorous triamide in hexamethylphosphoramide to give **14**. Total yield 10%, m.p. 308°C. ^{13}C NMR (DMSO-d_6): δ 101.2 (s), 116.9 (s), 118.5 (s), 141.7 (s) ppm. IR (KBr): 3393, 3313, 3209, 3046, 2221, 1649, 1509, 1432, 1316, 1251 cm^{-1}. Mass (*m/z*): 158 (M^+, 100%). UV-Vis (DMF) λ_{max} (log ε): 269 (4.20) and 424 (3.63) nm. F_{max}: (DMF) 516, (solid) 524 nm.

2-Amino-5-[[(dimethylamino)methylene]amino]-3,6-dicyanopyrazine (15) and 2,5-bis[[(dimethylamino)methylene]amino]-3,6-dicyanopyrazine (16a)

Compound (**2**) was stirred with dimethylformamide in the presence of oxalyl chloride in 1,4-dioxane, and heated under reflux for 2 h. After cooling, the solution was filtered, and the residue washed with water and dried. The component products were separated by column chromatography on silica gel using benzene as the eluent to give **15** and **16a**, respectively.

2-Amino-5-[[(dimethylamino)methylene]amino]-3,6-dicyanopyrazine (15)

Yield 31%, m.p. 247°C. ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 34.4 (q), 112.5 (s), 115.1 (s), 115.6 (s), 123.8 (s), 151.0 (s), 152.3 (s), 155.2 (d) ppm. ^1H NMR (DMSO-d_6/$CDCl_3$): δ 3.08 (3H, s, CH_3), 3.16 (3H, s, CH_3), 6.86 (2H, broad,

NH_2), 8.29 (1H, s, =CH−) ppm. IR (KBr): 3436, 3340, 3229, 2934, 2230, 1623, 1462, 1384, 1216 cm^{-1}. Mass (*m/z*): 215 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 310 (4.49) and 452 (3.84) nm. F_{max}: ($CHCl_3$) 527, (solid) 590 nm. Fluorescence quantum yield (Φ) 0.8.

Anal. Calcd. for $C_9H_9N_7$: C, 50.23; H, 4.22; N, 45.56%. Found: C, 50.02; H, 4.24; N, 45.41%.

2,5-Bis[[(dimethylamino)methylene]amino]-3,6-dicyanopyrazine (16a)

Yield 30%, m.p. 304°C. ^{13}C NMR ($CDCl_3$): δ 35.0 (q), 41.1 (q), 115.9 (d), 124.2 (s), 154.3 (s), 155.8 (s) ppm. ^1H NMR ($CDCl_3$): δ 3.17 (6H, s, CH_3), 3.18 (6H, s, CH_3), 8.49 (2H, s, =CH−) ppm. IR (KBr): 2932, 2232, 1615, 1452, 1364, 1210 cm^{-1}. Mass (*m/z*): 270 (M^+, 100%). UV-Vis ($CHCl_3$) λ_{max} (log ε): 344 (4.71) and 456 (3.91) nm. F_{max}: ($CHCl_3$) 525, (solid) 617 nm.

Anal. Calcd. for $C_{12}H_{14}N_8$: C, 53.32; H, 5.22; N, 41.46%. Found: C, 53.22; H, 5.20; N, 41.27%.

2,5-Bis[[(methylphenylamino)methylene]amino]-3,6-dicyanopyrazine (16b)

Yield 41%, m.p. 306°C. ^1H NMR ($CDCl_3$): δ 3.6 (6H, s, CH_3), 7.5 (10H, s, phenyl protons), 8.9 (2H, s, =CH−) ppm. IR (KBr): 3572, 2232, 1569, 1439, 1344, 1211 cm^{-1}. Mass (*m/z*): 394 (M^+). UV-Vis (MeCN) λ_{max} (log ε): 358 (4.78) and 440 (3.96) nm. F_{max}: (MeCN) 532 nm.

***S,S*-dimethyl-*N*-(2-amino-3,6-dicyanopyrazin-5-yl)sulfimide (17) and *S,S,S',S'*-tetramethyl-*N,N'*-(3,6-dicyanopyrazine-2,5-diyl)sulfimide (18)**

Compound (**2**, 2 mmol) was treated with dimethylsulfoxide (3 ml) and dichloromethane (1 ml) in the presence of oxalyl chloride (0.76 g) and triethylamine (1.8 g) at 10°C for 2 h. After quenching into ice water, the product was filtered, washed with water and methanol, and dried to give **17**. The filtrate was extracted with chloroform and the extract was subjected to column chromatography on silica gel using chloroform as eluent, to give **18**.

***S,S*-dimethyl-*N*-(2-amino-3,6-dicyanopyrazin-5-yl)sulfimide (17)**

Yield 5%, m.p. 205°C. ^{13}C NMR (DMSO-d_6/$CDCl_3$): δ 32.3 (q), 111.4 (s), 115.8 (s), 116.2 (s), 119.7 (s), 148.8 (s), 155.5 (s) ppm. ^1H NMR (DMSO-d_6/$CDCl_3$): δ 2.67 (6H, s, CH_3), 6.17 (2H, broad, NH_2) ppm. IR (KBr): 3474, 3355, 2223, 1615, 1446, 1377, 1228 cm^{-1}. Mass (*m/z*): 220 (M^+, 100%). UV-Vis (DMF) λ_{max} (log ε): 296 (4.36) and 513 (3.74) nm. F_{max}: (DMF) 613 nm.

Anal. Calcd. for $C_8H_8N_6S$: C, 43.62; H, 3.66; N, 38.16%. Found: C, 44.11; H, 3.74; N, 37.46%.

S,S,S',S'-tetramethyl-N,N'-(3,6-dicyanopyrazine-2,5-diyl)sulfimide (18)

Yield 59%, m.p. 234°C. ^{13}C MNR (DMSO-d_6): δ 32.6 (q), 117.1 (s), 117.7 (s), 155.1 (s) ppm. IR (KBr): 3399, 3005, 2217, 1640, 1412, 1345, 1227 cm^{-1}. Mass (*m/z*): 280 (M^+, 100%). UV-Vis (DMF) λ_{max} (log ε): 317 (4.35) and 526 (3.61) nm. F_{max}: (DMF) 651, (solid) 699 nm. Fluorescence quantum yield (Φ) < 0.1.

Anal. Calcd. for $C_{10}H_{12}N_6S_2$: C, 42.84; H, 4.31; N, 29.98%. Found: C, 42.72; H, 4.36; N, 29.65%.

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