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Dicyanopyrazine Studies. Syntheses and Characterization of New Bis-styryl Fluorescent Dyes from DAMN. Part III

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ABSTRACT

2-Bromomethyl-5,6-dicyano-3-phenylpyrazine **4** *was synthesized by the condensation reaction of DAMN* **3** *with 1-bromo-3-phenylpropane-2,3-dione 2. Wittig reaction of the 2-(triphenylphosphonium methyl) group of* **5** *with arylaldehydes or bisarylaldehydes gave new types of fluorescent styryl dyes. The PPPMO approach provides a reasonable correlation between calculated and experimental spectral data, and the MOPAC approach shows the optimized structure of dye chromophores. The substituent effects of dicyanopyrazines affecting their chemical, electronic, and physical properties were also studied. The electroluminescence properties of dye* **10c** *was also evaluated on the EL device. © 1998 Elsevier Science Ltd*

Keywords: dicyanopyrazine, pyrazinostyryl dye, fluorescent dye, MOPAC, electroluminescence.

INTRODUCTION

2,3-Dicyanopyrazine derivatives have become a potential subject of investigation because of their wide variety of applications, which include heterocycles for bioactive substances, coloring matters, nonlinear optical(NLO) and electroluminescence(EL) materials [1,2]. The styryl dyes derived from dicyanopyrazine have a rather small molecular size but have a strong donor–acceptor chromophoric system. They have strong fluorescence in solution

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and some have strong fluorescence even in solid state. These characteristics are very important in evaluating their NLO and EL properties.

In our previous paper [3], we synthesized some styryl dyes derived from diaminomaleonitrile (DAMN) and evaluated their spectral properties using the PPP MO and the MOPAC method. Some of these dyes showed a large solvatochromism, depending on the electrostatic interactions of the substituents at the 5-position of the 2,3- dicyanopyrazine moiety. These dyes are candidates for nonlinear optical materials because they produce a large dipole moment in the excited state.

In this paper, we report the syntheses and characterization of some styryl fluorescent dyes having a phenyl group at the 5-position of the 2,3-dicyanopyrazine system, and an evaluation of their functionalities with respect to their chemical structures.

RESULTS AND DISCUSSION

Wittig reaction of 6 with arylaldehydes

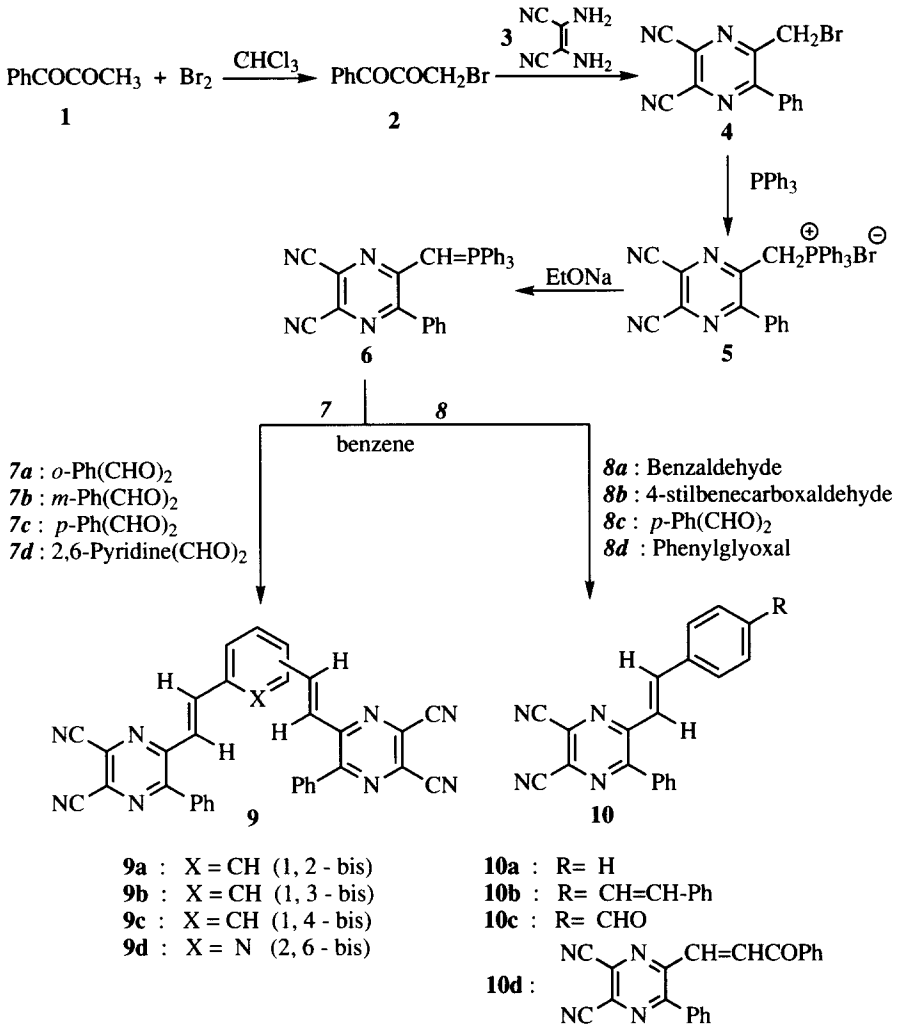
2,3-Dicyano-5-phenyl-6-triphenyl-phosphoniummethylpyrazine bromide **5** was synthesized in 50% yield by treatment of 2-bromomethyl-5,6-dicyano-3-phenylpyrazine **4** with triphenylphosphine, which in turn was obtained from diaminomaleonitrile (DAMN) via the reaction pathways shown in Scheme 1. 2,3-Dicyano-5-phenyl-6- triphenylphosphordiylmethylpyrazine **6**, which can be obtained by treatment of **5** with 1 equiv. sodium ethoxide in ethanol, reacts with arylaldehydes to give the bis styryl derivatives **9** and the styryl derivatives **10** in moderate yield.

Due to the strong electron withdrawing effect of the cyano groups on the pyrazine ring, the negative charge of the phosphorane **6** was delocalized into the dicyanopyrazine ring, thus resulting in a longer reaction time for the Wittig reaction of **6** with arylaldehydes [3]. Results are summarized in Table 1.

Visible and fluorescence spectra

The absorption and fluorescence maxima, both in solution and solid state, of compounds **9** and **10** are summarized in Table 2. The basic styryldicyanopyrazine dye **10a** has an intramolecular charge–transfer chromophoric system, from the results of PPP MO analysis [2].

Dye **10a**, as a standard, absorbed at 375 nm and substituent effects on the λ max were evaluated compared with this value. Dye **6** produced a bathochromic shift of 16 nm caused by the strong electron donating properties of its phosphordiylmethyl group. Dyes **9a** and **9b** absorbed at the same λ max



Scheme 1

TABLE 1
Wottog Reaction of **6** with Arylaldehydes

Run	*Reagent*	*Time(h)*	*Product*	*Yield(%)*
1	**7a**	25	**9a**	62
2	**7b**	25	**9b**	41
3	**7c**	40	**9c**	18
4	**7d**	40	**9d**	69
5	**8a**	13	**10a**	43
6	**8b**	10	**10b**	67
7	**8c**	6	**10c**	48
8	**8d**	4	**10d**	58

TABLE 2
Visible and Flourescence Spectra of 6~10

Compd.	*λmax(nm)*[a]	*Fmax ($CHCl_3$,nm)*[b]	*Fmax(solid, nm)*[c]	*ss*[d]	*ΔF*[e]
6	391	460	—	69	—
9a	366	480	516	114	36
9b	376	459	464	83	5
9c	340	467	507	127	40
9d	393	440	469	47	29
10a	375	466	482	91	16
10b	399	531	602	132	71
10c	339	451	549	112	98
10d	311	—	—	—	—

[a]in $CHCl_3$.
[b]Fluorescence maximum excited at λmax value.
[c]Fluorescence maximum excited at 360nm.
[d]Stoke's shift.
[e]ΔF = Fmax (solid)-Fmax(soln).

region but **9c** and **10c** showed a hypsochromic shift of 35 nm because of the electron withdrawing effect of the substituent. On the other hand, dye **10b** showed a bathochromic shift of 25 nm due to enlargement of the π conjugation. Intercept of the π-conjugation by the carbonyl group in **10d** produced a large hypsochromic shift of 65 nm.

Fluorescent maxium values (Fmax) of the dyes in solution and the solid state were quite different, and the Δ values were determined together with their Stoke's shift (S.S). The Fmax values in solution were observed around 440~480 nm, except for **10b** which emitted at 531 nm due to the larger π-conjugation. The S.S values are quite different from each other and ranged from 47 to 132 nm. As the S.S values indicate the energy loss in the excited state, dyes having smaller S.S values may efficiently convert their absorption energy to fluorescence. Dye **9d** has a small S.S value of 47 nm, but the other dyes showed values of 83~127 nm. Dyes **10a** **10c** showed quite large S.S values of 91~132 nm.

On the other hand, the Δ F values changed largely depending on the chemical structures and dye **10** (except for **10a**) generally showed larger Δ F

TABLE 3
Calculated Heat of Formation of Dyes **9b**, **9c** and **9d** in Each Conformational Structures.[a]

Dye	*A* (kcal mol^{-1})	*B* (kcal mol^{-1})	*C* (kcal mol^{-1})
9b	338.59	338.43	338.75
9c	338.40	340.37	338.55
9d	346.99	347.29	347.82

[a]Calculations were conducted by using MOPAC with PM 3 method.

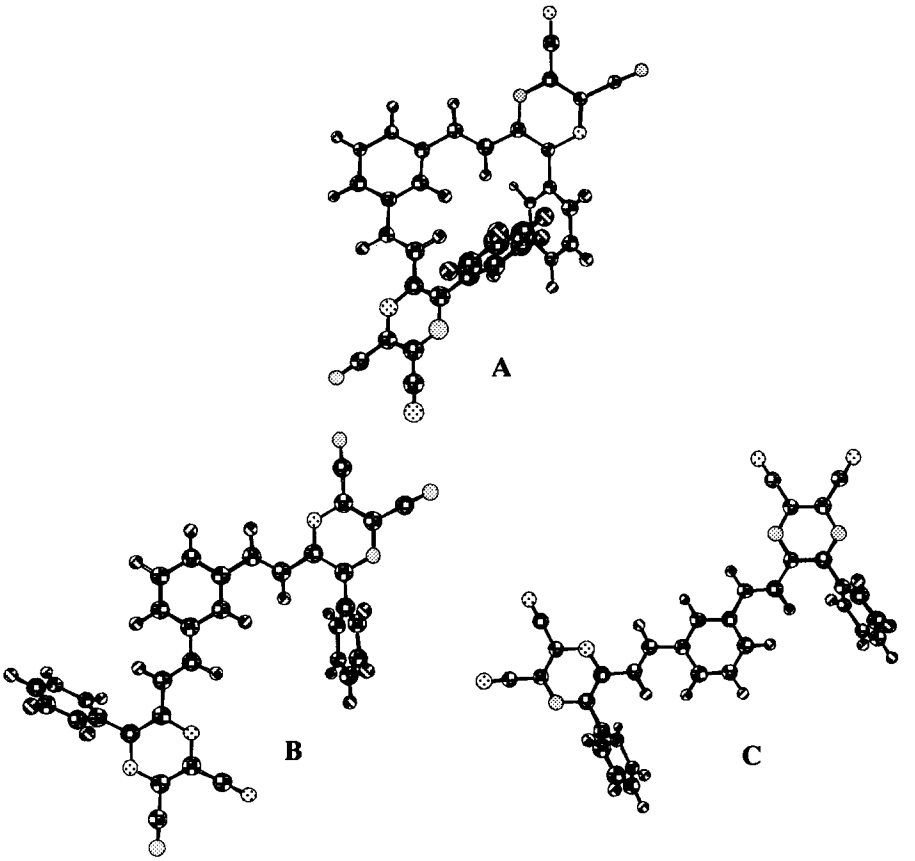
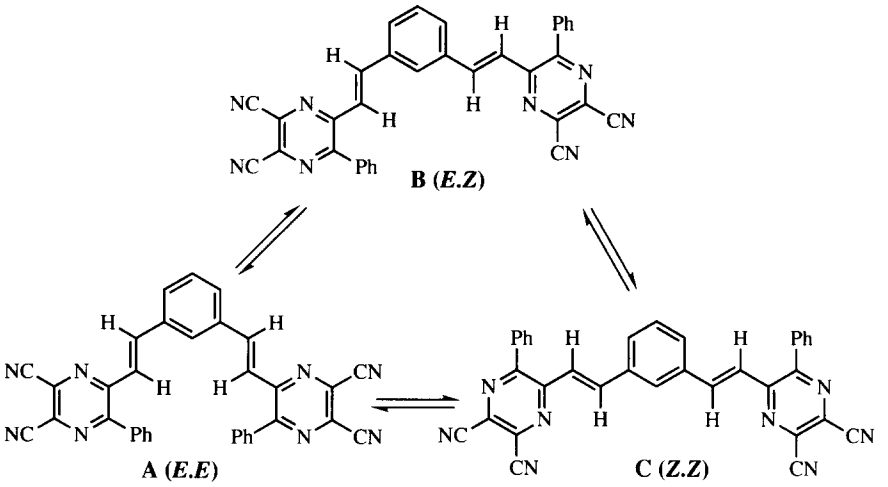


Fig. 1. Optimized conformational structures of **9b** by MOPAC with PM 3 calculations.

values than dye **9**. From these observations monostyryl dyes have more trends of stronger intermolecular interactions than bis-styryl dyes because of their complex dipole moments and steric requirements. It is of interest that dye **10** showed large Δ F values of around 100 nm, caused by their stabilization in the excited state in the solid state. Details of their molecular stacking in the solid state are now under investigation by X-ray crystal analysis and computer simulations and will be reported later.

Conformational analysis of dyes **9b**, **9c** and **9d** were conducted using the MOPAC with PM3 method; results are summarized in Scheme 2 and Table 3.

Dye **9a**, 1,2-bisstyrylpyrazine, was concluded to have a large steric hinderance between the styryl moieties, and the calculation therefore was not conducted. Dye **9b**, however, has a **trans** conformation against the vinyl groups, but has a different orientation between the central phenyl groups and the pyrazine-vinyl bond. These are defined as; A; *E.E*, B; *E.Z* and C; *Z.Z* as shown in Scheme 2.



Scheme 2

The calculated heats of formation (Δ H) were almost the same for each conformer, but **9d** has a larger Δ H value than the others and was much more stable than **9b** and **9c**, due to the electronic effect of the ring nitrogen in 9d. Dye 9d showed a larger λmax value and smaller Fmax and S.S. values compared with the other dyes in Table 2.

Optimization of each conformer for dye **9b** was also conducted by the MOPAC with PM 3 method.

In each conformer, an optimized structure was determined as shown in Fig. 1; the following observations were obtained. In the A conformer, the two phenyl groups were largely deviated to avoid their overlap, and consequently the two pyrazine moieties were also deviated slightly from the π-conjugated plane.

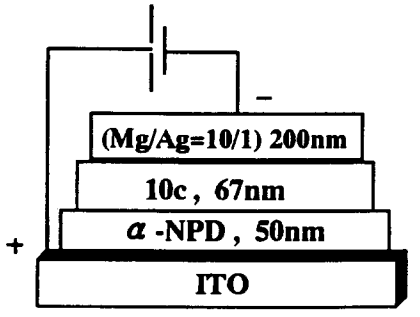


Fig. 2. EL device structure.

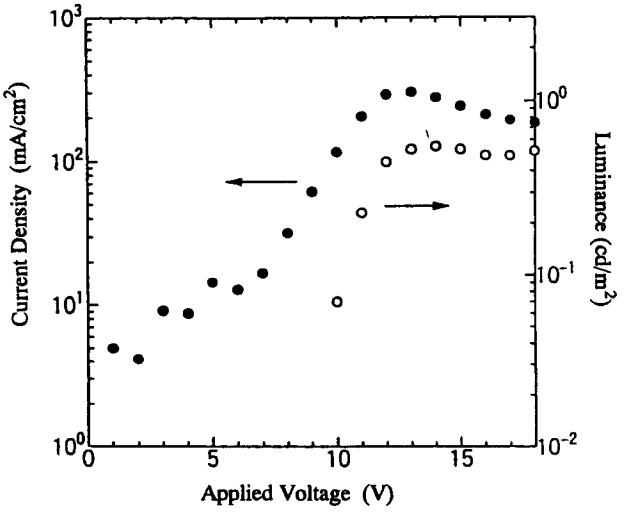


Fig. 3. Current density–voltage and luminance–voltage characteristics for the EL device (ITO/α-NPD/**10c**/MgAg).

On the other hand, B and C have planar structures except for the phenyl moieties. They are deviated from the π-plane by 59°, 63° in B, and 66°, 67° in C conformers, but little effect is evident on their λmax values. These phenyl groups in each conformer prevent intermolecular π–π· interactions of dye **9** in the solid state, which thus gives rather small Δ F values compared with those of dye **10** (Table 2).

Electroluminescent property of dye 10c

The electroluminescence (EL) device was fabricated by the conventional vacum deposition method. The charge-transporting material (α -NPD) and dye **10c** were deposited from a tungsten-boat onto an ITO coated glass substrate under 10^{-5}~10^{-6} Torr. The mixture of magnesium and silver (10:1) was then deposited from the tungsten-basket onto the dye deposited layer. The thicknesses of the charge transporting layer, emitting layer and cathode were 50, 67 and 200 nm, respectively, as shown in Fig. 2. Figure 3 shows the applied voltage dependence of the current density and the EL intensity of the EL device with **10c**. The maximum EL intensity of 0.55 cd m^{-2} was achieved at dc 14 volt and was observed only under dark conditions.

Compound **10c** exhibits a low reduction potential of −0.66 V, thus indicating a stronger electron withdrawing molecule compared with tris(8-quinolinato)aluminium, which showed a reduction potential of −1.79 V. Consequently, the low EL intensity of **10c** may arise from the imbalance of the energy gap between emitting and charge transporting materials [5].

EXPERIMENTAL

Identifications of compounds and measurements of properties were carried 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; ms spectra were recorded on an M-80 B Hitachi mass spectrometer; visible and fluorescence spectra were measured on a U-3410 Hitachi spectrophotometer and Shimadzu RF-5000 fluorescence spectrophotometer. Microanalysis was conducted with a Yanaco CHN MT-3 recorder. Geometry optimization of dyes was performed using the MOPAC 6.01 program [4] with the PM 3 Hamiltonians. All chemicals were reagent grade and were used without further purification unless otherwise specified.

6-Bromomethyl-5-phenyl-2,3-dicyanopyrazine (4)

A solution of bromine (5.3 ml), in chloroform (10 ml) was gradually added to a solution of 1-phenyl-1,2-propanedione **1**(50 mmole) in the same solvent (40 ml). After refluxing for 1 h, the solvent was removed partially *in vacuo*. The crude 3-bromo-1-phenyl- 1,2-propanedione **2** was dissolved in EtOH (15 ml) and added to a solution of DAMN **3** (50 mmole) in EtOH (30 ml).The reaction mixture was refluxed for 2.5 h and then cooled to 0°C. The resulting precipitate was collected by filtration and washed with ethanol. The crude product was recrystallized from ethanol to give **4** as a white solid (75%), mp 104~105°C; m/z 298 (M^+), 300 ($M^+ + 2$); ^{1}H nmr ($CDCl_3$); ^{1}H nmr (CDCl335) δ4.66 (2H, s, CH325Br), 7.63 (3H, m, phenyl protons), 7.80 (2H, m, phenyl protons).

Anal. Calcd. for $C_{13}H_7N_4Br$: C, 52.20; H, 2.36; N, 18.73. Found: C, 52.30; H, 2.43; N, 18.82.

2,3-Dicyano-5-phenyl-6-triphenylphosphordiylmethylpyrazine **(6)**

A solution of **4** (10 mmole) and triphenyl phosphine (10 mmole) in ethyl ether (60 ml) was stirred at room temperature for 27 h. The precipitated phosphonium salt **5** was filtered and washed with ethyl ether. To a stirred solution of **5** in EtOH (30 ml) under dry nitrogen at room temperature was added EtONa (10 mmole) in EtOH and the mixture was then stirred at room temperature for 0.5 h. The resulting precipitate was collected by filtration and washed with ethanol to give **6** as an orange solid (71%): mp 123~125°C; ^{1}H nmr (DMS0-d_6) δ4.01 (lH, s, CH=P), 7.83 (4H, m, phenyl protons), 8.10 (6H, m, phenyl protons), 8.40 (6H, m, phenyl protons), 8.65 (4H, m, phenyl protons).

Anal. Calcd. for $C_{31}H_{21}N_4P$: C, 77.49; H, 4.41; N, 11.66. Found: C, 77.66; H, 4.56; N, 11.56.

1,2-bis[2-(2,3-dicyano- 5-phenylpyrazino)ethenyl] benzene (**9a**)

A solution of 2,3-dicyano-5-phenyl-6-(triphenylphosphordiylmethyl) pyrazine **6** (2 mmoles) and *o*-phthalaldehyde (1 mmole) in benzene (10 ml) was refluxed under a nitrogen atmosphere and then cooled to room temperature. The resulting precipitate was filtered, washed with benzene and recrystallized from benzene to give **9a** as a pale yellow solid, mp 280~282°C; m/z 538 (M^+); ^{1}H nmr (DMSO-d_6)δ 8.32 (2H, d, *J* 15.6, CH=CH),7.71 (4H,m, phenyl protons), 7.52 (10H, m, phenyl protons), 7.19 (2H, d, *J* 15.6, CH=CH).

Anal. Calcd. for $C_{34}H_{18}N_8$: C, 75.83; H, 3.37; N,20.81. Found: C, 75.73; H, 3.54; N, 20.50.

The following compounds were synthesized by a similar method from **6** and the appropriate arylaldehyde.

1,3-Bis[2-(2,3-dicyano- 5-phenylpyrazino)ethenyl] benzene (**9b**).

mp 254~256° (benzene); m/z 538 (M^+); ^{1}Hnmr(DMSO-d_6) 8.17 (2H, d,*J* 15.6, CH=CH),7.74 (4H,m, phenyl protons), 7.58 (10H, m, phenyl protons), 7.34 (2H, d, *J* 15.6, CH=CH).

Anal. Calcd. for $C_{34}H_{18}N_8$: C, 75.83; H, 3.37; N,20.81. Found: C, 75.84; H, 3.56; N, 20.34.

1,4-Bis[2-(2,3-dicyano- 5-phenylpyrazino)ethenyl] benzene (**9c**).

mp > 300° (benzene); m/z 538 (M^+); ^{1}H nmr (DMSO-d_6) δ 7.75 (2H, d, *J* 15.6, CH=CH),7.68 (4H,m, phenyl protons), 7.55 (10H, m, phenyl protons), 7.23 (2H, d, *J* 15.6, CH=CH).

Anal. Calcd. for $C_{34}H_{18}N_8$: C, 75.83; H, 3.37; N,20.81. Found: C, 75.74; H, 3.41; N, 20.55.

2,6-Bis[2-(2,3-dicyano- 5-phenylpyrazino)ethenyl] pyridine (**9d**).

mp 258~259° (benzene); m/z 539 (M^+); ^{1}H nmr (DMSO-d_6)δ 8.01 (2H, d, *J* 15.6, CH=CH),7.70 (8H,m, phenyl protons), 7.50 (5H, m, phenyl protons), 7.45 (2H, d, *J* 15.6, CH=CH).

Anal. Calcd. for $C_{33}H_{17}N_9$: C, 73.46; H, 3.18; N, 23.36. Found: C, 73.14; H, 3.36; N, 22.99.

2,3-Dicyano-5-phenyl-6-(2-phenylethenyl)pyrazine (**10a**)

mp 190~191°(benzene); m/z 308 (M^+); ^{1}H nmr (DMSO-d_6)δ 7.57 (lH, d, *J* 15.9, CH=CH), 7.40 (10H, m, phenyl protons), 7.19 (H, d, *J* 15.9, CH=CH).

Anal. Calcd. for $C_{20}H_{12}N_4$: C, 77.91; H, 3.92; N, 18.17. Found: C, 77.80; H, 3.99; N, 17.94.

2,3-Dicyano-5-phenyl-6-[2-(4-styryl)ethenyl]pyrazine (**10b**).

mp 250~251° (benzene); m/z 410 (M^+); ^1H nmr (DMSO-d_6)δ 8.06 (lH, d, *J* 15.6, CH=CH),7.74 (2H,m, phenyl protons), 7.61 (9H, m, phenyl protons), 7.33 (6H, m, phenyl protons).

Anal. Calcd. for $C_{28}H_{18}N_4$: C, 81.93; H, 4.42; N, 13.65. Found: C, 82.15; H,4.56; N, 13.32.

2,3-Dicyano-5-phenyl-6-[2-(4-formylphenyl)ethenyl]pyrazine (**10c**).

mp 188~189° (benzene); m/z 336 (M^+); ^1H nmr (DMSO-d_6)δ 10.03 (lH, s, CHO), 8.21 (lH, d, *J* 15.6, CH=CH),7.70(9H, m, phenyl protons), 7.44 (lH, d, *J* 15.6, CH=CH).

Anal. Calcd. for $C_{21}H_{12}N_4O$: C, 74.99; H, 3.60; N, 16.66. Found: C, 75.00; H,3.86; N, 16.52

2,3-Dicyano-5-phenyl-6-[2-benzoylethenyl]pyrazine (**10d**).

mp 117~118° (benzene); m/z 336 (M^+); ^1H nmr (DMSO-d_6)δ 8.47 (lH, d, *J* 15.0, CH=CH), 8.11 (2H, d,*J* 6.9, phenyl protons), 7.93 (lH, d,*J* 15.0, CH=CH), 7.62 (8H, m, phenyl protons).

Anal. Calcd. for $C_{21}H_{12}N_4O$: C, 74.99; H, 3.60; N, 16.66. Found C, 74.92; H, 3.74; N, 16.66.

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REFERENCES

1. Hou, D., Oshida, A. and Matsuoka, M., *J. Heterocyclic Chem.*, 1993, **30**, 1571.
2. Jaung, J. Y., Matsuoka, M. and Fukunishi, K., *Dyes and Pigments*, 1996, **31**, 141.

3. Jaung, J. Y., Matsuoka, M. and Fukunishi, K., *Dyes and Pigments*, 1997, **34**, 255.
4. Stewart, J. J. P., *MOPAC* Ver. 6, QCPE No. 455; Hirano, T., *Revised MOPAC* Ver. 6.01 [*JCPE News letter*, 1991, **2**, 26].
5. Hosokawa, C., Higashi, H., Nakamura, H. and Kusumoto, T., *Appl. Phys. Lett.*, 1995, **67**, 3853.