Syntheses and Spectral Properties of 2,3,7,8-Tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine

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Base catalized intermolecular cyclization of 2-amino-3-chloro-5,6-dicyanopyrazines gave 5,10-disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **11-20**. These compounds have rather small molecular size but have strong intramolecular charge-transfer chromophoric system. They have strong fluorescence in solution and some have fluorescence even in the solid state which are very important to evaluate their electroluminescence property as an emitter for electroluminescence devices. The physical, structural, and electronic properties of these new 2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2'3'-*e*]pyrazines were studied using uv-visible spectroscopy and the Pariser-Parr-Pople molecular orbital calculation method.

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The chemistry of diaminomaleonitrile has been widely known for a long time since it was synthesized as a tetramer of hydrogen cyanide. Diaminomaleonitrile has been used to synthesize a wide variety of heterocycles for bioactive substance, dyes, *etc.* Dicyanopyrazine derivatives, which can be synthesized by the reaction of diaminomaleonitrile with α-diketones, are good synthetic reagents for coloring matters. In the previous paper, 2,3-dichloro-5,6-dicyanopyrazine, which was derived from diaminomaleonitrile with oxalyl chloride, was applied as fluorescence dyes and nonlinear optical materials [1]. Strong electron withdrawing ability of 5,6-dicyanopyrazine moiety makes possible nucleophilic substitution at the 2- and 3-positions. In the case of 2,3-dichloro-5,6-dicyanopyrazine, various nucleophiles such as amines, enamines and thiocarbonyl compounds could be used to synthesize many types of pyrazine heterocycles [2].

Cyanoaromatics and cyanoheteroaromatics generally have many useful properties and are interesting synthetic targets and undergo many unusual chemical reactions [3,4]. They act as strong electron acceptors to form intermolecular charge-transfer complexes for synthetic organic metals [3-5]. Molecules which have cyano groups have been incorporated into commercial fibers, carbon fibers, and thermally stable ladder polymers [6]. Cyanoheterocycles are the precursors for polymer crosslinking agents [7], chelating agents [7,8] and nonlinear optical materials [9].

Pyrazine has two nitrogen atoms at the 1,4-positions in the ring, and thus pyrazine coloring matters have additional functionalities compared with those of their benzene analogues. The special characteristics are a stronger donor-acceptor chromophoric system, higher polarizability, higher melting point and higher solubility in polar solvents. In particular, their strong fluorescence in the solid state becomes very important in order to evaluate their electroluminescence properties for electroluminescence devices. These characteristics can be applied in the molecular design for a variety of functional materials.

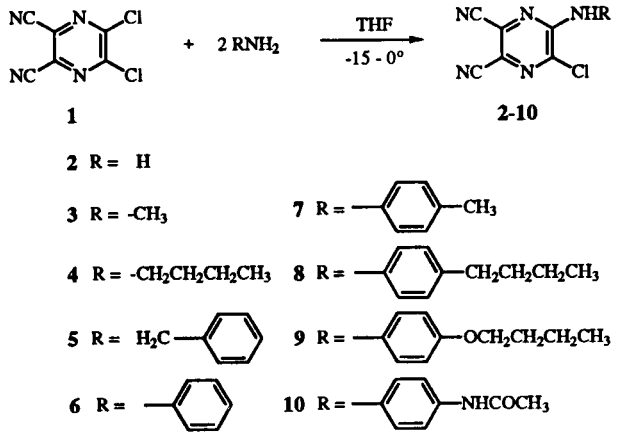
In this paper, 2-amino-3-chloro-5,6-dicyanopyrazines **2-10** were synthesized by nucleophilic substitution of 2,3-dichloro-5,6-dicyanopyrazine **1** with amines, and intermolecular cyclization of **2-10** in the presence of triethylamine gave 5,10-disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **11-20**. The physical, structural, and electronic properties of these new tetracyanodihydrodipyrazinopyrazines were investigated by using uv-visible spectroscopy and the Pariser-Parr-Pople molecular orbital calculation method.

Results and Discussion.

Syntheses of 2-Amino-3-chloro-5,6-dicyanopyrazines.

We have developed several methods for functionalizing 5,6-dicyanopyrazine derivatives. In our previous paper, nucleophilic substitutions of 2,3-dichloro-5,6-dicyanopyrazine (**1**) with various nucleophiles such as amines, enamines and thiocarbonyl compounds gave the corresponding 2- and 2,3-disubstituted pyrazines in good yields [1,2]. Due to the strong electron withdrawing effect of the cyano groups on the pyrazine ring, **1** should be favorable to undergo nucleophilic replacement at the carbon atom substituted by the chlorine atom. Treatment of **1** with two equivalents of amines in THF at low temperature afforded mono-alkyl or arylamino products in good yields (71-98%). The results are summarized in Scheme 1.

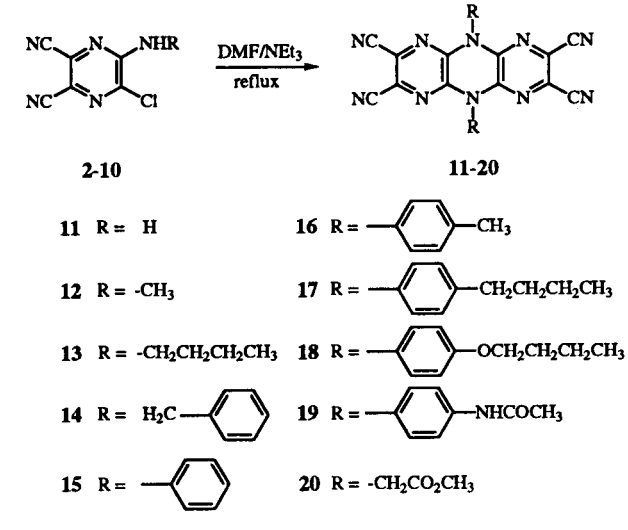
Scheme 1



Syntheses of 5,10-Disubstituted-2,3,7,8-tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazines **11-20**.

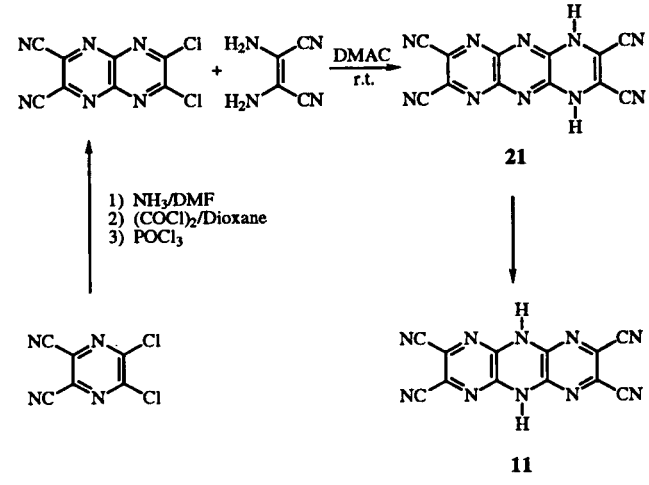
Synthesis of 2,3,7,8-tetracyano-5,10-dimethyl-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine **12** from reaction of **1** with 2,3-bis(*N*-methylamino)-5,6-dicyanopyrazine has been previously reported by us [1], but **12** was obtained in less than 5% yield. On the other hand, intermolecular cyclization of **2-10** in the presence of base gave **11-20** in moderate yields. The yields were improved when the reaction was carried out in DMF under reflux in the presence of two equivalents of triethylamine. The results are summarized in Scheme 2.

Scheme 2



An alternative synthesis of **11** is based on the condensation reaction of 2,3-dichloro-6,7-dicyano-1,4,5,8-tetraazanaphthalene [11] with diaminomaleonitrile in dimethylacetoamide (Scheme 3). This reaction gave two isomers of **11** and **21**, but **21** was unstable and spontaneously converted to **11** upon isolation by column chromatography on silica gel. Proton transfer of **21** to **11** was observed which might be due to the resonance stability of the dicyanopyrazine ring.

Scheme 3

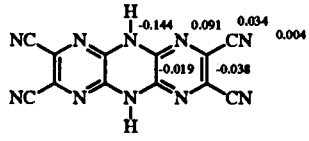


Visible and Fluorescence Spectra.

The results of Pariser-Parr-Pople molecular orbital calculations revealed that the basic structure **11** has a strong intramolecular charge-transfer chromophoric system in which the substituted amino group acts as a donor and two dicyanopyrazine rings act as acceptor moieties. The π-electron density changes accompanying the first excitation are shown in Figure 1. Compound **11** has a planer structure and the amino-nitrogen atoms have sp^2 hybridization from the results of *ab initio* calculation [10]. The absorption and fluorescence maxima of these compounds are summarized in Table 1 and were observed at 397-440 nm and 504-580 nm, respectively. Compound **11** produces bathochromic shift of 35-43 nm as compared with those of **12-20**, regardless of the fact that the hydrogen atom has less electron donating ability than the alkyl or aryl groups of **12-20**. This suggests that the amino protons of **11** are acidic, and consequently the nitrogen atoms donate their negative charge to the pyrazine rings. The acid-base equilibrium of **11** in aqueous ethanol with sodium ethoxide are shown in Figure 2. New absorption maximum at 458 and 487 nm were observed when base was added dropwise to **11**. It was found that the monoanion of **11** exists in aqueous ethanol but **11** became predominant in acidic ethanol (Figure 3).

Electrochemical Properties.

The cyclic voltammograms of tetracyanodihydrodipyrazinopyrazines were recorded in acetonitrile using



= NH Ionization Potential = 27.50 eV
= N– Ionization Potential = 12.60 eV
N■ Ionization Potential = 15.18 eV
λ max (Calcd.) = 411 nm
λ max (Obs.) = 440 nm

11

Figure 1. π-Electron density changes accompanying the first excitation of tetracyanodihydrodipyrazinopyrazine **11** by the Pariser-Parr-Pople Molecular Orbital calculation method.

Table 1

The Absorption and Fluorescence Properties of **11-20**

Compound	λ max (nm) [a]	F max (nm) [b]	SS [c]
11	440	580	140
12	398	504	106
13	402	526	114
14	397	516	119
15	405	530	125
16	402	521	119
17	397	518	121
18	399	520	121
19	400	527	127
20	398	516	118

[a] In Ethanol. [b] Fluorescence maximum excited at λ max value. [c] Stoke's Shift.

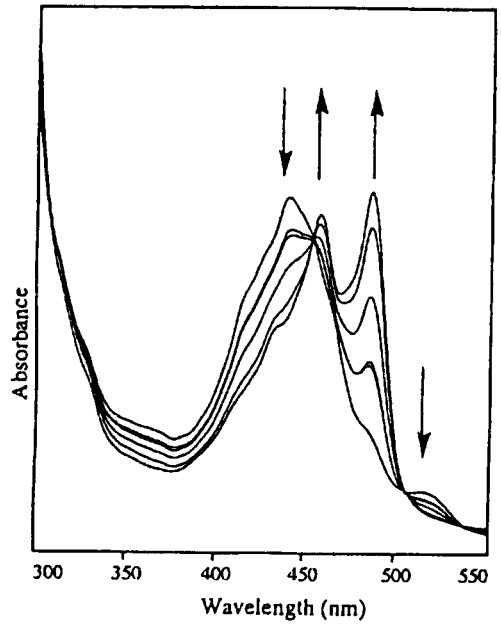


Figure 2. The proton dissociation effects of **11** with increasing concentration of base (sodium ethoxide) in ethanol.

0.1*M* Et_4NBF_4 as a supporting electrolyte which are summarized in Table 2. They showed reversible electrochemical properties which are very important to evaluate their electrochromism ability for electrochromic devices. The reduction potentials of tetracyanodihydrodipyrazinopyrazines range from -1.30 to -1.34V (Table 2). The magnitude of reduction potential depends on the nature of substituents R.

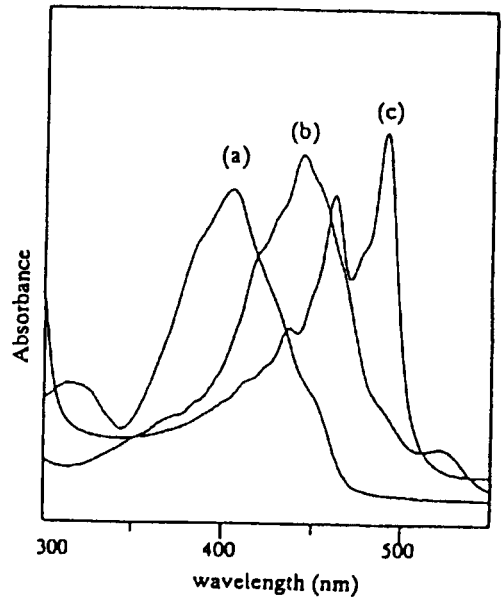


Figure 3. The acid-base dependence of the absorption spectra of **11** in ethanol; (a) acidic (*p*-toluenesulfonic acid) ethanol, (b) ethanol, (c) basic (sodium ethoxide) ethanol.

Table 2

The Reduction Potential of Tetracyanodihydrodipyrazinopyrazines

Compound	E(V) [a]	Reversibility
12	-1.34	rev.
15	-1.30	rev.
16	-1.30	rev.
17	-1.31	rev.
18	-1.32	rev.
19	-1.32	rev.

[a] Measured in CH_3CN vs Ag/Ag^+ with 0.1*M* Et_4NBF_4 as electrolyte. ref. = $Ag/AgNO_3$ Scan rate = 100mV/s.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro melting point apparatus without correction. The pmr spectra were taken on FT-NMR QE 300 MHz Shimadzu spectrometer. The ms spectra were recorded on a M-80 B Hitachi mass spectrometer. The visible and fluorescence spectra were measured on U-3410 Hitachi spectrophotometer and Shimadzu RF-5000 fluorescence spectrophotometer. Microanalysis was conducted with a Yanaco CHN MT-3 recorder. Cyclic voltammetry was done with a PAR Model 173 potentiostat/galvanostat. All chemicals were reagent grade and used without further purification unless otherwise specified. 2-Amino-3-chloro-5,6-dicyanopyrazine derivatives [1], 2,3-dichloro-6,7-dicyano-1,4,5,8-tetraazanaphthalene [11] were prepared by the known methods.

Syntheses of **2-10**.

To a solution of **1** (0.50 g, 2.5 mmoles) in dry tetrahydrofuran (5 ml) was added dropwise the amine (5 mmoles) at 0-5°, and

then the mixture was stirred at room temperature until all of **1** disappeared by tlc. The reaction solution was poured into 50 ml of water. The precipitated solid was filtered, washed with water and dried, to give the crude product **2-10**.

2-Amino-3-chloro-5,6-dicyanopyrazine (**2**).

The crude product was recrystallized from ethyl acetate/-*n*-hexane to give **2** as a pale yellow solid in 93% yield, mp 205-207°; ms: m/z 181 ([M+2]$^+$), 179 (M$^+$); ^{1}H nmr (DMSO-d_6): δ 8.92 (s, 2H, NH_2).

Anal. Calcd. for $C_6H_2N_5Cl$: C, 40.13; H, 1.10; N, 39.00. Found: C, 40.05; H, 0.91; N, 39.09.

2-Methylamino-3-chloro-5,6-dicyanopyrazine (**3**).

The crude product was recrystallized from ethyl acetate/-*n*-hexane to give **3** as a pale yellow solid in 81% yield, mp 186-187°; ms: m/z 195 ([M+2]$^+$), 193 (M$^+$); ^{1}H nmr (DMSO-d_6): δ 8.72 (s, 1H, NH), 2.88 (d, 3H, CH_3).

Anal. Calcd. for $C_7H_4N_5Cl$: C, 43.43; H, 2.08; N, 36.18. Found: C, 43.29; H, 1.99; N, 36.08.

2-*n*-Butylamino-3-chloro-5,6-dicyanopyrazine (**4**).

The crude product was recrystallized from carbon tetrachloride to give **4** as a white solid in 60% yield, mp 108-109°; ms: m/z 235 (M$^+$), 192 (M$^+$-$CH_2CH_2CH_3$); ^{1}H nmr (DMSO-d_6): δ 8.72 (t, 1H, NH), 3.37 (m, 2H, CH_2), 1.53 (quin, 2H, CH_2), 1.29 (m, 2H, CH_2), 0.86 (t, 3H, CH_3).

Anal. Calcd. for $C_{10}H_{10}N_5Cl$: C, 50.96; H, 4.28; N, 29.72. Found: C, 51.05; H, 4.31; N, 29.66.

2-Benzylamino-3-chloro-5,6-dicyanopyrazine (**5**).

The crude product was recrystallized from ethyl acetate to give **5** as a pale yellow solid in 71% yield, mp 130-132°; ms: m/z 271 ([M+2]$^+$), 269 (M$^+$); ^{1}H nmr (DMSO-d_6): δ 9.27 (t, 1H, NH), 7.30 (m, 5H, phenyl protons), 4.61 (d, 2H, CH_2).

Anal. Calcd. for $C_{13}H_8N_5Cl$: C, 57.90; H, 3.00; N, 25.97. Found: C, 57.63; H, 3.12; N, 25.79.

2-Anilino-3-chloro-5,6-dicyanopyrazine (**6**).

The crude product was recrystallized from ethanol to give **6** as a pale yellow solid in 98% yield, mp 175-176°; ms: m/z 257 ([M+2]$^+$), 254 ([M-1]$^+$); ^{1}H nmr (DMSO-d_6): δ 10.18 (s, 1H, NH), 7.54-7.23 ((d + t + t), 5H, phenyl protons).

Anal. Calcd. for $C_{12}H_6N_5Cl$: C, 56.38; H, 2.37; N, 27.39. Found: C, 56.27; H, 2.36; N, 28.45.

2-(4'-Methylphenyl)amino-3-chloro-5,6-dicyanopyrazine (**7**).

The crude product was recrystallized from ethyl acetate/-*n*-hexane to give **7** as a pale yellow solid in 98% yield, mp 181-182°; ms: m/z 270 ([M+1]$^+$), 268 ([M-1]$^+$); ^{1}H nmr (DMSO-d_6): δ 10.13 (s, 1H, NH), 7.45-7.27 ((d + d), 4H, phenyl protons), 2.44 (s, 3H, CH_3).

Anal. Calcd. for $C_{13}H_8N_5Cl$: C, 57.90; H, 3.00; N, 25.97. Found: C, 57.81; H, 2.99; N, 25.90.

2-(4'-*n*-Butylphenyl)amino-3-chloro-5,6-dicyanopyrazine (**8**).

The crude product was recrystallized from ethyl acetate/-*n*-hexane to give **8** as a pale yellow solid in 86% yield, mp 163-164°; ms: m/z 311 (M$^+$), 267 (M$^+$-$CH_2CH_2CH_3$); ^{1}H nmr (DMSO-d_6): δ 10.12 (s, 1H, NH), 7.43-7.24 ((d + d), 4H, phenyl protons), 2.56 (t, 2H, CH_2), 1.53 (quin, 2H, CH_2), 1.29 (m, 2H, CH_2), 0.87 (t, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{19}N_5Cl$: C, 60.66; H, 6.05; N, 22.11. Found: C, 60.51; H, 6.17; N, 22.23.

2-(4'-*n*-Butoxylphenyl)amino-3-chloro-5,6-dicyanopyrazine (**9**).

The crude product was recrystallized from ethanol to give **9** as a pale yellow solid in 61% yield, mp 143-144°; ms: m/z 329 (M$^+$), 239 (M$^+$-$OCH_2CH_2CH_2CH_3$); ^{1}H nmr (DMSO-d_6): δ 10.10 (s, 1H, NH), 7.40-6.98 ((d + d), 4H, phenyl protons), 3.97 (t, 2H, CH_2), 1.67 (quin, 2H, CH_2), 1.42 (m, 2H, CH_2), 0.90 (t, 3H, CH_3).

Anal. Calcd. for $C_{16}H_{19}N_5OCl$: C, 57.74; H, 5.75; N, 21.04. Found: C, 57.94; H, 5.66; N, 20.89.

2-(4'-Acetamidophenyl)amino-3-chloro-5,6-dicyanopyrazine (**10**).

The crude product was recrystallized from ethanol to give **10** as a pale yellow solid in 90% yield, mp >300°; ms: m/z 312 (M$^+$), 270 (M$^+$-$COCH_3$); ^{1}H nmr (DMSO-d_6): δ 10.13-10.02 ((s + s), 2H, 2NH), 7.60-7.44 ((d + d), 4H, phenyl protons), 2.02 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_9N_5OCl$: C, 53.77; H, 2.90; N, 26.87. Found: C, 53.60; H, 3.02; N, 26.77.

Syntheses of **11-19**.

A solution of **2-10** (2 mmoles) and triethylamine (4.4 mmoles) in dimethylformaldehyde (10 ml) was refluxed for 10 hours and poured into aqueous 1 *M* hydrochloric acid. The precipitate was filtered, washed with water and dried, to give the crude product **11-19**.

Synthesis of **11** by the Alternate Method.

A solution of 2,3-dichloro-6,7-dicyano-1,4,5,8-tetraazanaphthalene (2 mmoles) and diaminomaleonitrile (2 mmoles) in *N,N*-dimethylacetamide (10 ml) was stirred at room temperature for 48 hours and then poured into water, the precipitate was filtered, washed with water and dried, to give the crude product **11**.

2,3,7,8-Tetracyano-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**11**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate) and recrystallized from ethyl acetate:acetonitrile, giving **11** as red crystals (78%), mp >300°; ms: m/z 286 (M$^+$), 284 (M$^+$-2H); ^{1}H nmr. The proton nmr of **11** in DMSO-d_6 and perdeuteriomethanol did not show the NH proton peak because of its strong deprotonation property.

Anal. Calcd. for $C_{12}H_2N_{10}$: C, 50.34; H, 0.70; N, 48.96. Found: C, 50.27; H, 1.26; N, 48.09.

2,3,7,8-Tetracyano-5,10-dimethyl-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**12**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate:*n*-hexane, 3:2, v/v) and recrystallized from ethyl acetate, giving **12** as yellow crystals (43%), mp >300°; ms: m/z 314 (M$^+$); ^{1}H nmr (DMSO-d_6): δ 3.15 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{14}H_6N_{10}$: C, 53.51; H, 1.92; N, 44.57. Found: C, 53.22; H, 1.89; N, 44.30.

2,3,7,8-Tetracyano-5,10-di(*n*-butyl)-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**13**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate:*n*-hexane, 6:1, v/v) and recrys-

tallized from ethyl acetate, giving **13** as yellow crystals (37%), mp 268-269°; ms: m/z 398 (M^+), 355 (M^+-$CH_2CH_2CH_3$); ^1H nmr (DMSO-d_6) δ 3.79 (t, 4H, $2CH_2$), 1.55 (quin, 4H, $2CH_2$), 1.40 (m, 4H, $2CH_2$), 0.94 t, 6H, $2CH_3$).

Anal. Calcd. for $C_{20}H_{18}N_{10}$: C, 60.29; H, 4.55; N, 35.18. Found: C, 59.95; H, 4.55; N, 34.76.

2,3,7,8-Tetracyano-5,10-dibenzyl-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**14**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate:*n*-hexane, 2:1, v/v) and recrystallized from ethyl acetate, giving **14** as yellow crystals (46%), mp >300°; ms: m/z 466 (M^+); ^1H nmr (DMSO-d_6): δ 7.45 (m, 10H, phenyl protons), 5.02 (s, 4H, $2CH_2$).

Anal. Calcd. for $C_{26}H_{-4}N_{10}$: C, 66.95; H, 3.03; N, 30.03. Found: C, 66.56; H, 3.08; N, 29.41.

2,3,7,8-Tetracyano-5,10-diphenyl-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**15**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate:*n*-hexane, 1:1, v/v) and recrystallized from ethyl acetate, giving **15** as yellow crystals (38%), mp >300°; ms: m/z 438 (M^+), 437 (M^+-H); ^1H nmr (DMSO-d_6): δ 7.69 (m, 10H, phenyl protons).

Anal. Calcd. for $C_{24}H_{10}N_{10}$: C, 65.75; H, 2.30; N, 31.95. Found: C, 65.14; H, 2.55; N, 31.05.

2,3,7,8-Tetracyano-5,10-di(4'-methyl phenyl)-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**16**).

The crude product was purified by column chromatography on silica gel (eluent toluene:methylene chloride, 5:1, v/v) and recrystallized from ethyl acetate, giving **16** as orange crystals (49%), mp >300°; ms: m/z 466 (M^+), 465 (M^+-Me); ^1H nmr (DMSO-d_6): δ 7.42-7.23 ((d + d), 8H, phenyl protons), 2.41 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{26}H_{14}N_{10}$: C, 66.95; H, 3.03; N, 30.03. Found: C, 66.68; H, 3.07; N, 29.11.

2,3,7,8-Tetracyano-5,10-di(4'-*n*-butylphenyl)-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**17**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate:*n*-hexane, 1:1, v/v) and recrystallized from ethyl acetate, giving **17** as orange crystals (61%), mp 295-297°; ms: m/z 550 (M^+), 549 (M^+-H); ^1H nmr (DMSO-d_6): δ 7.47-7.25 ((d + d), 8H, phenyl protons), 2.71 (t, 4H, $2CH_2$), 1.69 (quin, 4H, $2CH_2$), 1.43 (m, 4H, $2CH_2$), 0.96 (t, 6H, $2CH_3$).

Anal. Calcd. for $C_{32}H_{36}N_{10}$: C, 68.55; H, 6.47; N, 24.98. Found: C, 68.45; H, 6.47; N, 24.78.

2,3,7,8-Tetracyano-5,10-di(4'-*n*-butoxyphenyl)-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**18**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate:*n*-hexane, 1:1, v/v) and recrystallized from ethyl acetate, giving **18** as orange crystals (36%), mp >300°; ms: m/z 582 (M^+), 470 (M^+-2Bu); ^1H nmr (DMSO-d_6): δ 7.33-7.16 ((d + d), 8H, phenyl protons), 4.06 (t, 4H, $2CH_2$), 1.79 (quin, 4H, $2CH_2$), 1.51 (m, 4H, $2CH_2$), 0.98 (t, 6H, $2CH_3$).

Anal. Calcd. for $C_{32}H_{32}N_{10}O_2$: C, 64.85; H, 6.12; N, 23.63. Found: C, 65.01; H, 5.58; N, 23.88.

2,3,7,8-Tetracyano-5,10-di(4'-acetamidophenyl)-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**19**).

The crude product was purified by column chromatography on silica gel (eluent ethyl acetate) and recrystallized from acetonitrile, giving **19** as yellow crystals (45%), mp > 300°; ms: m/z 552 (M^+), 519 (M^+-$COCH_3$); ^1H nmr (DMSO-d_6): δ 10.22 (s, 2H, 2NH), 7.80-7.25 ((d + d), 8H, phenyl protons), 2.09 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{28}H_{16}N_{12}O_2$: C, 60.87; H, 2.92; N, 30.42. Found: C, 60.43; H, 2.98; N, 29.98.

2,3,7,8-Tetracyano-5,10-di(methylacetato)-5,10-dihydrodipyrazino[2,3-*b*:2',3'-*e*]pyrazine (**20**).

A solution of **2** (2 mmoles) and methyl bromoacetate (6 mmoles) in acetone (30 ml) was refluxed in the presence of triethylamine (4.4 mmoles) for 22 hours. The solvent was removed *in vacuo*, and the residue was submitted to column chromatography on silica gel (eluent ethyl acetate) and recrystallized from ethyl acetate, giving **20** as yellow crystals (30%), mp 218-219°; ms: m/z 430 (M^+), 371 (M^+-CO_2Me); ^1H nmr (DMSO-d_6): δ 4.83 (s, 4H, $2CH_2$), 3.86 (s, 6H, $2CH_3$).

Anal. Calcd. for $C_{18}H_{10}N_{10}O_4$: C, 50.00; H, 2.33; N, 32.40. Found: C, 50.94; H, 2.59; N, 32.57.

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