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Reaction of 2,3-Dichloro-5,6-dicyanopyrazine with Amines

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ABSTRACT

*Reaction of 2,3-dichloro-5,6-dicyanopyrazine (**1**) with amines gave mono-substituted or bis-substituted products (**2a–h**). Reaction of **1** with thioacetamide as well as 2,3-bis(N-methylamino)-5,6-dicyanopyrazine (**2c**) gave 1,4,6,9-tetraaza-2,3,7,8-tetracyanothianthrene (**5**) or 2,3,7,8-tetracyano-1,4,6,9-tetraaza-5,10-dimethyl-5,10-dihydrophenazine (**6**), respectively. Non-linear optical properties for **2a–h** as well as biological activity of **4a** were evaluated.*

1 INTRODUCTION

2,3-Dichloro-5,6-dicyanopyrazine (**1**) (Scheme 1)[1] is of interest as a potential intermediate for industrial use and can be produced from diaminomaleonitrile (DAMN) and oxalic acid chloride. The chemistry of DAMN has been known for a long time since it was synthesized as a tetramer of hydrogen cyanide. Due to the strong electron-withdrawing effect of the cyano groups on the pyrazine ring, **1** should be favourable to undergo nucleophilic replacement of the carbon atom substituted by the chlorine atom. In order to evaluate functionalized properties of products based on nucleophilic substitution on **1**, SHG (Second Harmonic Generation) properties and biological activity were studied. We selected a variety of amines and other nucleophiles as reagents and synthesized mono- or bis-substituted products.

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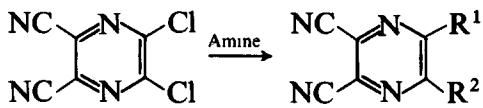
2 RESULTS AND DISCUSSION

Because of the strong electron-deficient character on the pyrazine ring, **1** is very favourable to nucleophilic replacement. Treatment of **1** with amines in acetone or in benzene at room temperature afforded bis-alkylamino or mono-alkylamino products (**2a–h**) in good yields (74–92%). The results are summarized in Scheme 1 and Table 1.



1 **2a–h**

	2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	**2h**
R^1	NH_2	NH_2	NHMe	NEt_2	NHBu-n	NMe_2	Pyrrolidino	Morpholino
R^2	Cl	NH_2	NHMe	NEt_2	NHBu-n	NMe_2	Cl	Cl

Scheme 1

The identification for **2a–h** was based on ^{1}H-NMR data, elemental analyses, IR and mass spectra (see Experimental section). From the IR spectra of **2a–h**, the stretching vibrations of CN for all of the products prepared were observed as sharp and strong absorption bands appearing in the narrow range between 2214 and 2237 cm^{-1}. In general, owing to the unsymmetry of the molecule of mono-substituted compounds (**2a**, **2g** and **2h**), characteristic stretching vibrations of the two CN groups on the molecule should show some differences. However, these differences were not observed in mono-substituted compounds. Molecular ions of mass spectra

TABLE 1
Reaction of **1** with Amines[a]

Run	*Reactant*	*Reagent*	*Molar ratio* (1/amine)	*Time* (*h*)	*Product*	*Yield* (%)
1	**1**	25% aq NH_3	1:2	2	**2a**	76
2	**1**	25% aq NH_3	1:4	4	**2b**	75
3	**1**	40% aq $MeNH_2$	1:4	2	**2c**	90
4	**1**	Et_2NH	1:4	4	**2d**	74
5	**1**	NH_2Bu-*n*	1:4	0·5	**2e**	90
6	**1**	Me_2NH	1:2	3	**2f**	87
7	**1**	Pyrrolidine	1:2	0·2	**2g**	80
8	**1**	Morpholine	1:2	0·2	**2h**	92

[a] To **1** (10 mmol) in acetone or benzene was dropwise added amine (20 or 40 mmol), and then the mixture was stirred at room temperature.

TABLE 2
SHG Efficiencies and UV/VIS Data for **2a–h**

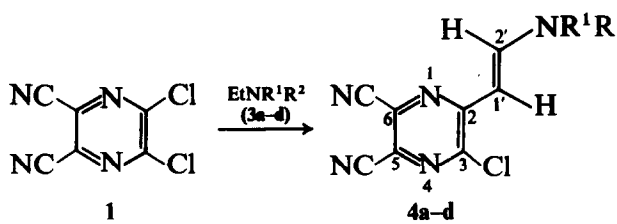
Compd	*M.p.* (°C)	*UV/VIS*[a] λ_{max} (*nm*)	*SHG*[b]
2a	208	336, 282	>1 U
2b	>330	320	x
2c	313–315	319	1 U
2d	93–94	357	x
2e	154	324	x
2f	57–58	316	x
2g	86–87	314	x
2h	88–89	317	x

[a] Measured in $CHCl_3$.
[b] Powder efficiency. x, not detected.

for **2a–h** as well as ^{1}H-NMR data obtained are all in agreement with the structures depicted.

SHG properties of **2a–h** as non-linear optical materials were evaluated and the results are given in Table 2. Compounds **2a** and **2c** have powder efficiencies of 1 U against urea in the solid states, but lost their activities after being melted. The other compounds did not show any SHG properties, either in the solid state or after being melted.

On the other hand, we found that **1** could react with triethylamine (**3a**) to give a novel aminovinyl-substituted product: 2-(2′-diethylaminovinyl)-3-chloro-5,6-dicyanopyrazine (**4a**) in 25% yield (Scheme 2). It was proposed that oxidation of **3a** by **1** to diethylvinylamine, which reacted quickly with **1**,



1 4a–d

	R^1	R^2
4a	Et	Et
4b	Me	Me
4c	—$(CH_2)_4$—	
4d	—$(CH_2)_2O(CH_2)_2$—	

Scheme 2

afforded **4a**. In addition, it has been reported that reaction of chloranil with **3a** also afforded an aminovinyl-substituted product.[2] From these results, it was found that **1** had an oxidation property similar to chloranil.

Characterization of the structure of **4a** is based upon ^{1}H-NMR spectral data (Table 3) as well as elemental analysis, IR and mass spectra. H–C(1′) and H–C(2′) (as an AB system) were split into a doublet, appearing in the range 5·50–5·55 ppm (d, $J = 12{\cdot}21$ Hz) and 8·11–8·15 ppm (d, $J = 12{\cdot}21$ Hz) respectively. According to the coupling constant of the ethylene protons ($J = 12{\cdot}21$ Hz), **4a** should exist in a trans-configuration. Due to strong resonance conjugation from the amino group to the pyrazine ring, rotation of the C(2′)–N single bond is completely restricted at room temperature, and the chemical shifts for the two ethyl groups should therefore show some differences. The chemical shifts of CH_2 for one of the N-ethyl groups appeared at 3·53–3·61 ppm (q, 2H), and the other at 3·43–3·51 ppm (q, 2H). Chemical shifts of methyl groups for two N-ethyl groups overlapped with each other and appeared in the range of 1·22–1·16 ppm (t + t, 6H). The ^{1}H-NMR spectrum of **4a** is shown in Fig. 1.

Evaluation of the scope of this reaction revealed that practical synthetic applications are rather limited. Although a variety of tertiary amines was tried, few satisfactory results were obtained. On the whole, the yields of the reactions were very poor. Treatment of N,N-dimethylethylamine (**3b**), N-ethylpyrrolidine (**3c**), as well as N-ethylmorpholine (**3d**) gave the desired products **4b–d** in poor yields, less than 5% (Scheme 2), respectively. The

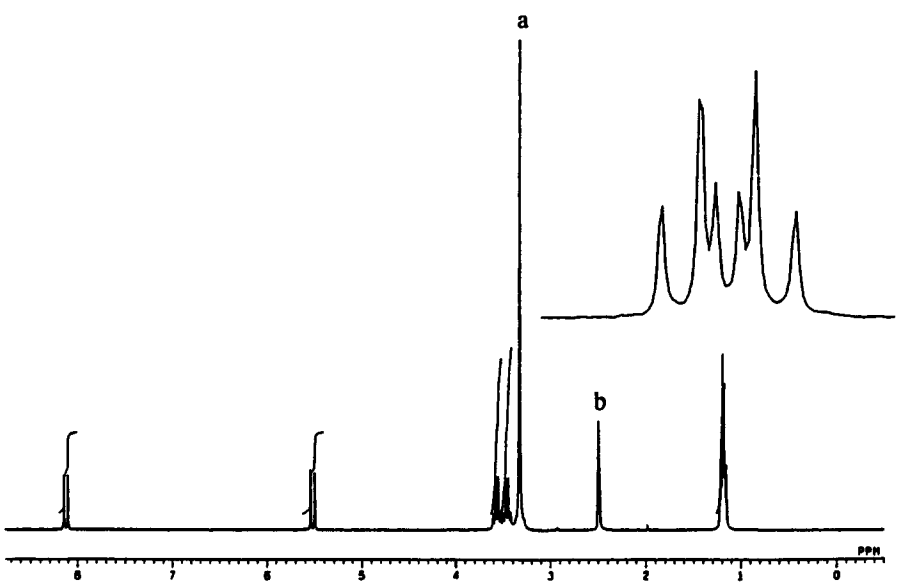


Fig. 1. ^{1}H-NMR spectrum of **4a** in DMSO-d_6: (a) H_2O; (b) DMSO.

TABLE 3
Spectral Data for **4a–d**

Compd	*Ir* (cm^{-1})[a]	*PMR* (δ *in ppm*)	*MS* (*m/z, rel. int. %*)
4a[b]	2220 (CN)	8·11–8·15 (d, 12·11, 1H); 5·50–5·55 (d, 12·11, 1H); 3·53–3·61 (q, 2H); 3·43–3·51 (q, 2H); 1·22–1·16 (t + t, 6H)	263 (32, $[M+2]^+$), 261 (100, M^+), 246 (38), 232 (25), 226 (30)
4b[c]	2226 (CN)	8·04–8·09 (d, 12·11, 1H); 5·44–5·49 (d, 12·11, 1H); 3·31 (s, 3H); 3·07 (s, 3H)	235 (19, $[M+2]^+$), 233 (57, M^+), 218 (22), 198 (100)
4c[c]	2224 (CN)	8·23–8·28 (d, 12·09, 1H); 5·40–5·44 (d, 12·28, 1H); 3·68–3·73 (t, 2H); 3·39–3·45 (t, 2H); 2·00–2·17 (m, 4H)	261 (17, $[M+2]^+$), 259 (51, M^+), 224 (100)
4d[c]	2224 (CN)	8·00–8·04 (d, 12·82, 1H); 5·60–5·65 (d, 12·82, 1H); 3·81–3·85 (t, 4H); 3·55 (s, 4H)	277 (32, $[M+2]^+$), 275 (100, M^+) 240 (83), 218 (51), 182 (68), 155 (29), 129 (12), 85 (39)

[a] On KBr pellet.
[b] In DMSO-d.
[c] In $CDCl_3$ with reference to TMS.

results of the reaction, as well as spectral data, are summarized in Tables 3 and 4.

The structure assignments for **4b–d** were also established on the basis of ^{1}H-NMR data (Table 3), IR and mass spectra as well as elemental analyses. In the case of **4b**, H–C(1′) and H–C(2′) (as an AB system) were split into a doublet, appearing in the range 5·44–5·49 ppm (d, $J = 12{\cdot}21$ Hz) and 8·04–8·09 ppm (d, $J = 12{\cdot}21$ Hz), respectively. The chemical shifts for two N–CH_3 showed some differences appearing at 3·07 and 3·31 ppm, respectively. In the case of **4c**, H–C(1′) and H–C(2′) (as an AB system) were split into a doublet

TABLE 4
Reaction of **1** with Tertiary Amines[a]

Run	*Reactant*	*Reagent*	*Time* (*h*)	*Product*	*Yield* (%)
9	**1**	**3a**	24	**4a**	25
10	**1**	**3b**	24	**4b**	2
11	**1**	**3c**	48	**4c**	4
12	**1**	**3d**	48	**4d**	2

[a] A mixture of **1** (7·5 mmol) and tertiary amine (**3a–d**) (15 mmol) in DMF (30 ml) was stirred at room temperature.

at 5·40–5·44 ppm (d, $J = 12·09$ Hz) and 8·23–8·28 ppm (d, $J = 12·28$ Hz), respectively. The chemical shifts for the two CH_2 attached to the N atom of the pyrrolidine moiety showed different values, viz. 3·68–3·73 ppm (t, 2H) and 3·39–3·45 ppm (t, 2H), respectively, due to the restriction of rotation of the C(2′)–N single bond at room temperature. Chemical shifts of H–C(3″) and H–(5″) on the pyrrolidine moiety also showed some differences, appearing at 2·00–2·17 ppm. In the case of **4d**, the proton for N–CH_2 was normally split into a triplet, but the proton for O–CH_2 which was also expected to be split into a triplet, appeared as a broad peak (270 MHz-NMR). According to the coupling constants of the ethylene protons of the products, **4b–d** also exist in trans-configurations. Data for UV/VIS and fluorescence spectra of **4a–d** are shown in Table 5.

Proton NMR spectra of **4c** were measured at different temperatures in order to investigate the relationship between the structure and temperature (Fig. 2). From the spectra, the chemical shifts and coupling constants of the ethylene protons did not change with increase in temperature. This indicates that the trans-configuration of **4c** did not change between room temperature and 150°C. On the other hand, the chemical shifts of H–C(2″) and H–C(5″) on the pyrrolidine moiety of **4c**, with two separate sets of peaks, eventually overlapped with increase in temperature and became finally a singlet at 110°C. Those for H–C(3″) and H–C(4″) on the pyrrolidine moiety of **4c** showed the same tendency, and a single peak was observed above 90°C. This implies that the N–C single bond begins to rotate with increase in temperature.

The biological activity of **4a** was evaluated.[3] Preliminary test results showed that **4a** possesses an effectiveness in controlling some types of plant diseases. On the basis of this evaluation, we are studying further the development of new products of this class and trying to improve the yield of the reaction. Some satisfactory results have been achieved by using enamines as reagents.[4]

TABLE 5
Spectral Data of UV/VIS and Fluorescence for **4a–d**[a]

Compd	*UV/VIS* λ_{max} (*nm* (*log* ε)	λ_{ex}[b] (*nm*)	F_{max}[c] (*nm*)	*Fluorescence* (*rel. int. %*)
4a	407 (4·60)	360	522	21
4b	401 (4·53)	401	517	83
4c	415 (4·61)	370	523	15
4d	404 (4·52)	514	514	100

[a] In $CHCl_3$.
[b] λ_{ex}, excitation maximum.
[c] F_{max}, fluorescence maximum.

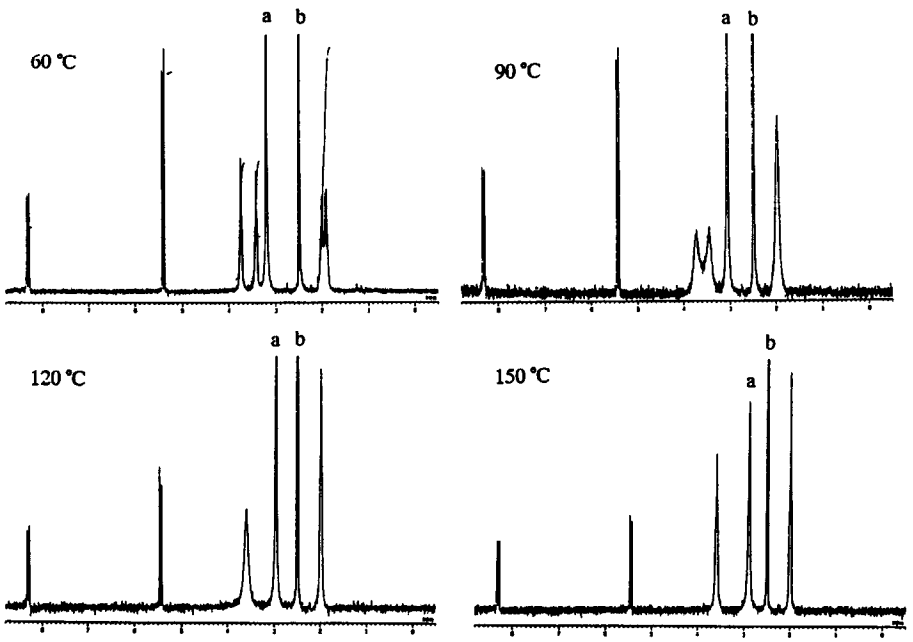
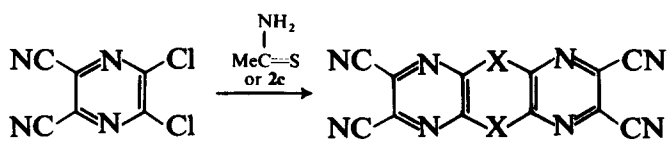


Fig. 2. ^{1}H-NMR spectrum of **4c** in DMSO-d_6 at different temperatures: (a) H_2O; (b) DMSO.

On the other hand, treatment of **1** with thioacetamide in DMF gave 1,4,6,9-tetraaza-2,3,7,8-tetracyanothianthrene (**5**) in excellent yield (97%) (Scheme 3). Synthetic methods for this type of compound from ortho-dihalogenoheterocycles and thiocarbonyl compounds have been previously reported by us.[5] Compound **5** is a known compound, prepared by a different synthetic route, and it has been reported that **5** has some bactericidal and fungicidal activities.[6] Reaction of **1** with 2,3-bis(N-methylamino)-5,6-dicyanopyrazine (**2c**) afforded 2,3,7,8-tetracyano-1,4,6,9-tetraaza-5,10-dimethyl-5,10-dihydrophenazine (**6**) in poor yield of less than 5%. The identification of the structure for **5–6** is based upon NMR, IR and MS spectra as well as elemental analyses. The ^{13}C-NMR spectrum for **5** showed three different kinds of carbons appearing at 113·5, 131·5 and 155·4 ppm, respectively, which is reasonable due to the symmetry of the molecule. The 1H-NMR spectrum for **6** showed a singlet at 3·15 ppm (N–CH_3). Mass spectra for **5** and **6** gave strong molecular ions at 320 and 314, respectively.



1 **5** X = S; **6** X = NMe

Scheme 3

3 EXPERIMENTAL SECTION

3.1 General

M.p.: YANACO MP-500D apparatus, uncorrected. IR spectra: SHIMADZU IR-420 and HORIBA FT-200 spectrophotometer; wavenumbers at absorption maxima in cm^{-1}. NMR spectra: JOEL JNM-GX (270 MHz) spectrometer; chemical shifts in ppm with reference to TMS. Mass spectra: SHIMADZU LKB-9000 and FINNIGAN MAT TSQ-70 spectrometers; expressed in forms of fragment ion and relative intensity (%). UV/VIS spectra: SHIMADZU UV-265FS and UV-3100 spectrophotometer; wavelengths in nm and molar extinction coefficients in log ε. Microanalysis was conducted on YANACO CHN MT-3 recorder.

3.2 Syntheses of 2a–h

To **1** (1·99 g, 10 mmol) dissolved in acetone or benzene (50 ml) was added the amine (20 or 40 mmol) at 0–5°C, and the reaction mixture was then stirred at room temperature until the starting materials had completely disappeared (TLC). The salt formed was filtered out and the filtrate was evaporated to dryness. The residue was submitted to column chromatography on silica gel using EtOAc as eluent.

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

MS (*m/z*):	181 (35, $[M+2]^+$), 179 (100, M^+), 152 (24), 144 (32).
$C_6H_2N_5Cl$ (179·57)	Calcd C40·13 H1·1 N39·00%
	Found C41·05 H0·73 N39·96%
^{1}H-NMR (DMSO-d_6):	8·92 (s, 1H); 8·87 (s, 1H)
UV/VIS (MeOH):	336, 282 nm
IR (KBr):	3476, 3358, 2237, 1622, 1389 cm^{-1}

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

MS (*m/z*):	160 (100, M^+), 133 (58), 106 (17)
$C_6H_4N_6$ (160·14)	Calcd C45·00 H2·52 N52·48%
	Found C44·74 H2·47 N52·75%
1H-NMR (DMSO-d_6):	7·55 (s, 4H)
UV/VIS (MeOH):	319, 226 nm
IR (KBr):	3332, 3161, 2229, 1666, 1524, 1088 cm^{-1}

*2,3-Bis(N-methylamino)-5,6-dicyanopyrazine (**2c**)*

MS (*m/z*):	188 (100, M^+), 173 (24), 146 (21), 119 (14)
$C_8H_8N_6$ (188·12)	Calcd C51·06 H4·28 N44·66%
	Found C51·37 H4·15 N44·91%
^{1}H-NMR (DMSO-d_6):	7·73 (s, 1H); 7·71 (s, 1H), 2·91 (s, 3H); 2·90 (s, 3H)
UV/VIS (MeOH):	319 nm
IR (KBr):	3386, 2229, 1576, 1412, 1088 cm^{-1}

*2,3-Bis(N,N-diethylamino)-5,6-dicyanopyrazine (**2d**)*

MS (*m/z*)	272 (71, M^+), 243 (100), 213 (8), 199 (19), 158 (12
$C_{14}H_{20}N_6$ (272·35)	Calcd C61·74 H7·40 N30·86%
	Found C62·33 H7·49 N31·13%
^{1}H-NMR ($CDCl_3$):	3·53–3·45 (q, 8H); 1·10–1·05 (t, 12H)
UV/VIS (MeOH):	356, 258 nm
IR (KBr):	2978, 2935, 2875 (s), 2227, 1520, 1489, 1458, 1348, 1252 cm^{-1}

*2,3-Bis(N-butylamino)-5,6-dicyanopyrazine (**2e**)*

MS (*m/z*):	272 (100, M^+), 229 (37), 215 (27), 200 (31), 1·73 (79), 109 (20)
$C_{14}H_{20}N_6$ (272·35)	Calcd C61·74 H7·40 N30·87%
	Found C61·76 H7·43 N30 85%
^{1}H-NMR ($CDCl_3$):	5·58 (s, 1H); 5·57 (s, 1H); 3·54–3·47 (m, 4H); 173–1·62 (m, 4H); 1·50–1·37 (m, 4H); 0·99–0·93 (t, 6H)
UV/VIS (CH_2Cl_2):	324 nm
IR (KBr):	3390, 2954, 2931, 2862, 2227, 1585, 1560 cm^{-1}

*2-N,N-Dimethylamino-3-chloro-5,6-dicyanopyrazine (**2f**)*

MS (*m/z*):	209 (34, $[M+2]^+$, 207 (100, M^+), 192 (90), 178 (38), 165 (18), 129 (48), 76 (42)
$C_8H_6N_5Cl$ (207·62)	Calcd C46·28 H2·91 N33·73%
	Found C45·53 H2·60 N33·69%
^{1}HNMR ($CDCl_3$):	3·38 (s, 6H)
UV/VIS (CH_2Cl_2):	316 nm
IR (KBr):	2214, 1576, 1516, 1419, 1396, 1313, 1190, 1122, 1090, 1036, 916, 762, 613, 488 cm^{-1}

*2-Pyrrolidino-3-chloro-5,6-dicyanopyrazine (**2g**)*

MS (*m/z*):	235 (16, $[M+2]^+$), 233 (52, M^+), 204 (100) 178 (27)

$C_{10}H_8N_5Cl$ (233·66)	Calcd C51·40 H3·45 N29·97%
	Found C51·11 H3·14 N30·64%
^{1}H-NMR ($CDCl_3$):	3·90–3·86 (q, 4H); 2·07–2·02 (m, 4H)
UV/VIS (CH_2Cl_2):	314 nm
IR (KBr):	2226, 1558, 1506, 1454, 1387, 1336, 1244, 1147, 1119, 1078, 1034, 910, 486, 419 cm^{-1}

*2-Morpholino-3-chloro-5,6-dicyanopyrazine (**2h**)*

MS (*m/z*):	251 (35, $[M+2]^+$), 249 (88, M^+), 234 (51), 214 (57), 206 (85), 191 (82), 164 (100), 129 (45), 110 (33), 76 (43)
$C_{10}H_8N_5ClO$ (249·66)	Calcd C48·11 H3·23 N28·05%
	Found C48·16 H3·02 N28·52%
^{1}H-NMR ($CDCl_3$):	3·88–3·85 (t, 4H); 3·82–3·78 (t, 4H)
UV/VIS (MeOH):	317, 211 nm
IR (KBr):	2233, 1543, 1497, 1444, 1371, 1259, 1169, 1132, 1117, 1014, 906, 623, 492 cm^{-1}

3.3 Syntheses of 4a–d

To **1** (1·5 g, 7·5 mmol) dissolved in DMF (30 ml) was added dropwise a tertiary amine (**3a–d**) (15 mmol) at room temperature, and the reaction mixture was then stirred until all materials had reacted (TLC). The salt formed was filtered out, and the filtrate was evaporated to dryness. The residue was submitted to column chromatography on silica gel with EtOAc as eluent.

*2-(2′-Diethylaminovinyl)-3-chloro-5,6-dicyanopyrazine (**4a**)*

M.p.	146–148°C
MS (*m/z*):	263 (32, $[M+2]^+$), 261 (100, M^+), 246 (38), 232 (25), 226 (30)
$C_{12}H_{12}N_5Cl$ (261·71)	Found C54·77 H4·36 N26·80%
	Calcd C55·07 H4·62 N26·76%
^{1}H-NMR (DMSO-d_6):	See Table 3
UV/VIS (MeOH):	See Table 5
IR (KBr):	2220, 1610, 1520, 1450, 1381, 1254 cm^{-1}

*2-(2′-Dimethylaminovinyl)-3-chloro-5,6-dicyanopyrazine (**4b**)*

M.p.	178–183°C
MS (*m/z*):	235 (19, $[M+2]^+$), 233 (57, M^+), 218 (22), 198 (100)

$C_{10}H_8N_5Cl$ (233·66)	Calcd C51·40 H3·45 N29·97%
	Found C51·05 H3·65 B29·55%
^{1}H-NMR ($CDCl_3$):	See Table 3
UV/VIS ($CHCl_3$):	See Table 5
IR (KBr):	2226, 1624, 1531, 1458, 1421, 1373, 1259, 1090, 1036, 879, 789, 613, 474 cm^{-1}

*2-(2'-Pyrrolidinovinyl)-3-chloro-5,6-dicyanopyrazine (**4c**)*

M.p.	181–182°C
MS (*m/z*):	261 (17, $[M+2]^+$), 259 (51, M^+), 224 (100)
$C_{12}H_{10}N_5Cl$ (259·70)	Calcd C55·50 H3·88 N26·79%
	Found C55·33 H3·71 N26·85%
^{1}H-NMR ($CD3l_3$):	See Table 3
UV/VIS (CH_2Cl_2):	See Table 5
IR (KBr):	2224, 1616, 1531, 1448, 1396, 1379, 1254, 1090, 1036, 795, 474 cm^{-1}

*2-(2'-Morpholinovinyl)-3-chloro-5,6-dicyanopyrazine (**4d**)*

M.p.	209–210°C
MS (*m/z*):	277 (32, $[M+2]^+$), 275 (100, M^+), 240 (83), 218 (51), 182 (68), 155 (29), 129 (12), 85 (39)
$C_{12}H_{10}N_5ClO$ (275·70)	Calcd C52·28 H3·66 N25·40%
	Found C52·63 H3·89 N25·78%
^{1}H-NMR ($CDCl_3$):	See Table 3
UV/VIS ($CHCl_3$):	See Table 5
IR (KBr):	2224, 1606, 1525, 1458, 1383, 1315, 1271, 1236, 1194, 1090, 1024, 808 cm^{-1}

3.4 1,4,6,9-Tetraaza-2,3,7,8-tetracyanothianthrene (5)

A mixture of **1** (5 mmol) and thioacetamide (5 mmol) in DMF (10 ml) was stirred at 20°C for 3 h. The reaction mixture was poured into water (100 ml) and the precipitate was collected. On recrystallization from acetone/$CHCl_3$, the product was obtained in 97% yield as yellow needles.

M.p. > 320°C	
MS (*m/z*): 320 (100, M^+)	
$C_{12}N_8S_2$ (320·31)	Calcd C45·00 H34·98%
	Found C44·80 H34·53%
^{13}C-NMR (acetone-d_6):	113·5, 131·5, 155·4
UV/VIS (EtOH):	273 (33 800), 373 (13 560)
IR (KBr):	2239, 1506, 1321, 1321·0, 1236, 1163, 1088, 1001, 739, 590 cm^{-1}

3.5 2,3,7,8-Tetracyano-1,4,6,9-tetraaza-5,10-dimethyl-5,10-dihydrophenazine (6)

To a mixture of **2c** (0·188 g, 1 mmol) and **1** (0·199 g, 1 mmol) in DMF (10 ml) was dropwise added Et_3N (0·20 g, 2 mmol) at 80°C. After maintaining at 80°C for 2 h, the reaction mixture was heated to 100–110°C for 2 h and then at 130–140°C for another 16 h. After removing the solvent, the residue was submitted to column chromatography on silica gel using EtOAc as eluent, Compound **6** (10 mg) was obtained as a yellow solid.

MS (*m/z*):	314 (100, M^+), 299 (30)
^{1}H-NMR (DMSO-d_6):	3·15 (s, 6H)
UV/VIS (MeOH):	404, 318, 253 nm
IR (KBr):	2925, 2233, 1581, 1542, 1473, 1354, 1172, 1088 cm^{-1}

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