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Syntheses and Properties of New Styryl Dyes Derived from 2,3-Dicyano-5-methylpyrazines

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ABSTRACT

*Reaction of 2,3-dicyano-5-methylpyrazine derivatives (**3a–e**) with arylaldehydes gave new fluorescent styryl dyes (**4–8**). These styryl dyes have extended π-conjugated systems and are strong intramolecular charge-transfer chromophoric systems. They are of interest as non-linear optical materials, which should produce a large dipole moment in the excited state, and consequently induce large dipole moment differences accompanying laser irradiation. The styryl dyes derived from 2,3-dicyano-6-hydroxy-5-methylpyrazine showed large solvatochromism, depending on the polarity of the solvent, due to tautomerism between the hydroxypyrazine and the pyridone forms. The fluorescence and solvatochromism properties of dyes **4–8** were also studied, and structure–property relationships in solution and in the solid state were evaluated on the basis of molecular stacking in the solid state. Copyright © 1996 Elsevier Science Ltd*

INTRODUCTION

The reaction of diaminomaleonitrile (DAMN, **1**) with 1-methyl-1,2-dicarbonyl compounds (**2**) gave 2,3-dicyano-5-methylpyrazine derivatives (**3**) which have biological activity for controlling certain plant diseases.[1] DAMN, a weakly basic diamine resembling *o*-phenylenediamine in reactivity, can be

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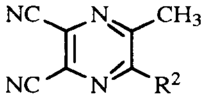
prepared directly from hydrogen cyanide by oligomerization[2] and indirectly by hydrogenation of diiminosuccinonitrile.[3] DAMN has been used to prepare a variety of heterocyclic compounds, including 4,5-dicyanoimidazoles,[4] 2,3-dicyanopyrazines[2,5] and purines.[6] The herbicidal properties of a series of 2,3-dicyanopyrazines have been evaluated by Nakamura and co-workers.[7] Our research group has been interested in the chemistry of nitrile-containing molecules for many years. In particular, we have been interested in how nitrile substitution affects the chemical, electronic and physical properties of pyrazines. We have synthesized these compounds and studied their properties. Our previous work[8] has been carried out with respect to conformational studies concerning the structural isomerism of dicyanopyrazine dyes with intramolecular charge-transfer character. In order to obtain new insights into the chemistry and properties of these compounds from an organic materials perspective, this work is concerned with the design, synthesis and characterization of new styryl dyes based on 2,3-dicyano-5-methylpyrazines of general formula **3**.



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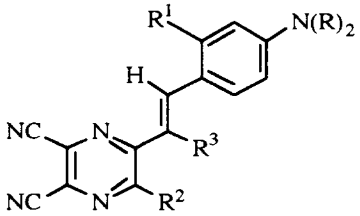
$R^2 = H, CH_3, OH, OAc$



4~8

$R^1 = H, OH, CH_3$

$R^3 = H, COOH$

The intention was also to synthesize some donor–acceptor type styryl dyes (**4**–**8**) which additionally have the ability to form intermolecular π–π interactions between the π molecular plane of each molecule. These dyes should show large differences in λ_{max} between solution and solid state, due to the strong π–π intermolecular interactions. We found that some of the new dyes satisfied these requirements. These produced large dipole moments in the excited state, and consequently induced large dipole moment differences on laser irradiation, a necessary requirement for non-linear optical materials.[9]

Styryl dyes with intramolecular charge-transfer character were synthesized, and their conformational analyses with respect to tautomerism were evaluated using visible spectra and PPP–MO calculations. Their fluorescence properties and solvatochromism were also studied to evaluate structure–property relationships in solution and in the solid state.

RESULTS AND DISCUSSION

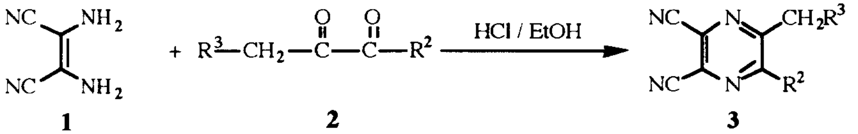
Condensation reaction of compound 3 with arylaldehydes

2,3-Dicyano-5-methylpyrazines (**3**) were readily obtained by the condensation reaction of DAMN (**1**) with 1-methyl-1,2-dicarbonyl compounds (**2**). The results are summarized in Scheme 1 and Table 1.

The ^1H NMR spectra showed that the methyl protons of compound **3** were observed at around 2.3–2.8 ppm, while those of toluene were observed at 2.09 ppm. Due to the strong electron-withdrawing effect of the cyano groups on the pyrazine ring, the methyl group of compound **3** was able to undergo a condensation reaction with arylaldehydes. Reactions of compound **3** with *N*,*N*-dimethylaminobenzaldehyde, 4-(*N*,*N*-diethylamino)-2-methylbenzaldehyde and *N*,*N*-diethylaminosalicylaldehyde gave the corresponding styryl dyes **4–8**, but in less than 30% yields (Scheme 2, Table 2).

Visible and fluorescence spectra

The PPP-MO calculation results revealed that the basic chromophore of the styryl dyes (**9**) has a strong intramolecular charge-transfer system in which the dialkylaminophenyl group acts as a donor moiety and the dicyanopyrazine group acts as an acceptor moiety. The π-electron density changes



1 **2** **3**

Scheme 1.

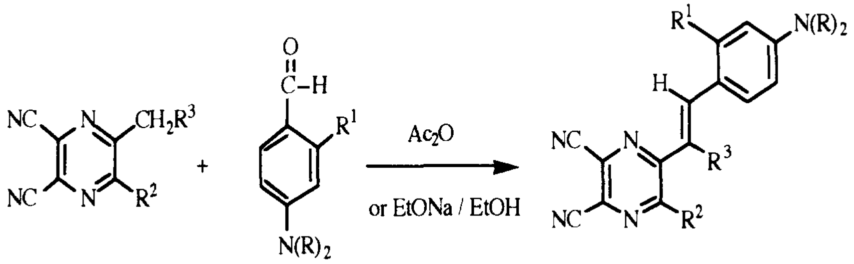
TABLE 1
2,3-Dicyano-5-methylpyrazine derivatives

Compound	*R^2*	*R^3*	*Reaction time (h)*[a]	*^1H NMR (δCH_3) (ppm)*	*Yield (%)*
3a	OH	H	4.0	2.43 (DMSO-D_6)	85.0
3b[b]	OAc	H	3.0	2.32 (DMSO-D_6)	85.0
3c	CH_3	H	3.5	2.72 ($CDCl_3$)	81.9
3d	H	H	3.5	2.79 ($CDCl_3$)	83.7
3e	OH	COOH	4.0	4.46 (DMSO-D_6)[c]	24.0

[a] DAMN (10 mmoles) and compound **2** (10 mmoles) in EtOH (15 ml) were stirred in the presence of 4 N HCl (6 ml).

[b] *O*-Acetylation reaction of compound **3a** in 10 equivalents of Ac_2O.

[c] Methylene proton in the CH_2COOH group.



3

4~8

Scheme 2.

TABLE 2

Syntheses of Styryl Dyes

Compound	*R*	*R^1*	*R^2*	*R^3*	*Method*[a]	*Reaction time (h)*	*Yield (%)*
4a	Me	H	OH	H	A	36	28.7
4b	Et	Me	OH	H	A	36	11.8
4c	Et	OH	OH	H	C	0.5	89.6
5a	Me	H	OAc	H	B	2	24.3
5b	Et	Me	OAc	H	B	2	47.6
5c	Et	OH	OAc	H	B	2	21.8
6a	Me	H	Me	H	B	10	15.1
6b	Et	Me	Me	H	B	10	16.7
6c	Et	OH	Me	H	B	10	6.6
7a	Me	H	H	H	B	10	22.0
7b	Et	Me	H	H	B	10	23.8
7c	Et	OH	H	H	B	10	7.2
8	Me	H	OH	COOH	A	36	54.9

[a] See experimental section for general procedures.

accompanying the first excitation are shown in Fig. 1. Table 3 shows the fluorescence and visible spectra data of compounds **4**–**8**. The absorption and fluorescence maxima of these dyes were observed at 491–580 nm and 575–610 nm, respectively. Stoke's shifts were 55–90 nm, except for dye **4c** which showed a smaller value of 30 nm. The electronic character of the substituents in Fig. 1 strongly reflects the experimental results in donor–acceptor systems. The bathochromic shifts of 117–142 nm in compounds **4**–**7** compared with compound **8** are attributed to the lower electron withdrawing ability of the group at the R^3 position. Substitution of an acceptor at the R^3 position (causing a decrease in electron density) may be expected to produce large hypsochromic shifts in λ_{max}. Similarly, substitution of a donor group in a position at which there is an electron density decrease should produce a bathochromic shift of λ_{max}, and vice versa.

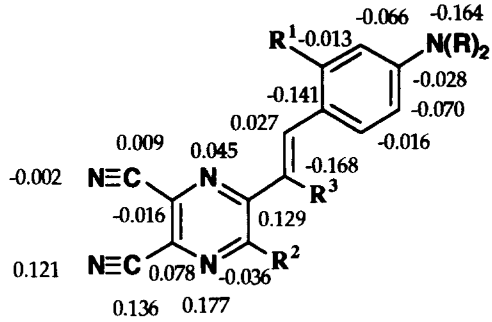


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Fig. 1. π-Electron density changes accompanying the first excitation of styryl dye **9**.

TABLE 3
Visible and Fluorescence Spectra of Dyes **4–8**

Compound	λ_{max} *(nm)*[a]	$\Delta\lambda$[b]	F_{max} *(nm)*[c]	*SS*[d]
4a	498	—	575	77
4b	491	−7	590	99
4c	580	82	610	30
5a	523	—	582	59
5b	543	20	598	55
5c	531	8	—	—
6a	499	—	583	84
6b	520	21	598	78
6c	498	−1	582	84
7a	499	—	598	99
7b	523	24	605	82
7c	507	8	592	85
8	425	—	479	54

[a] In $CHCl_3$.
[b] $\Delta\lambda = \lambda_X - \lambda_a$.
[c] Fluorescence maximum excited at λ_{max} value.
[d] Stoke's shift.

Solvatochromism and tautomerism of dyes 4–8

Solvent effects on dyes **4–8** in their visible absorption and fluorescence spectra are shown in Tables 4 and 5. The λ_{max} values of compounds **5–8** showed bathochromic shifts with an increase in the solvent polarity, and these compounds thus have a larger dipole moment in the excited state than in the ground state. On the other hand, the λ_{max} of dye **4** showed a hypsochromic shift with increasing solvent polarity, which is unusual for such an intramolecular charge-transfer chromophoric system. Dye **4** has a hydroxyl group at the 3-position in the pyrazine ring and tautomerism between the

TABLE 4
Solvent Effects on Visible Spectra of Dyes **4**–**8**

Compound	*1,4-Dioxane (nm)*	*$CHCl_3$ (nm)*	*CH_3CN (nm)*	*DMSO (nm)*	*MeOH (nm)*	$\Delta\lambda^a$
4a	498	498	449	451	449	−49
4b	552	491	470	464	470	−83
4c	561	580	554	475	471	−90
5a	503	523	517	527	515	12
5b	534	543	540	549	540	6
5c	514	531	523	531	521	7
6a	476	499	485	495	480	4
6b	496	520	509	520	508	12
6c	481	498	486	490	487	6
7a	476	499	483	491	477	1
7b	499	523	508	518	510	11
7c	483	507	487	495	486	3
8	410	425	428	432	415	5

$^a\Delta\lambda = \lambda_{\mathrm{MeOH}} - \lambda_{\mathrm{Dioxane}}$.

TABLE 5
Fluorescence Spectra of Dyes **4**–**8**

Compound	*1,4-Dioxane (nm)*	*$CHCl_3$ (nm)*	*CH_3CN (nm)*	*DMSO (nm)*	*MeOH (nm)*	$SS_{max}{}^a$
4a	575	575	540	560	575	126
4b	590	590	560	580	590	120
4c	603	610	580	565	565	120
5a	570	582	—	—	540	136
5b	580	598	—	—	593	55
5c	585	—	—	—	—	71
6a	578	583	—	—	—	102
6b	598	598	—	—	—	102
6c	570	582	—	—	—	89
7a	576	598	—	—	—	100
7b	588	605	—	—	—	89
7c	575	592	—	—	—	92
8	470	479	482	507	498	75

[a] The maximum Stoke's shift value in solvents.

hydroxypyrazine form **A** and pyridone form **B** is possible. It was found that tautomers of compound **4** existed in solution, and that the equilibrium was greatly influenced by the polarity of the solvent. The observed large solvatochromism of dye **4** (Table 4) was attributed to this tautomerism, but dyes **5**–**8** did not show this phenomenon because of the absence of the hydroxyl group. The colour of dye **4** in solution changed dramatically from yellow in polar solvents to scarlet in non-polar solvents (Fig. 2). Tautomer **A** was

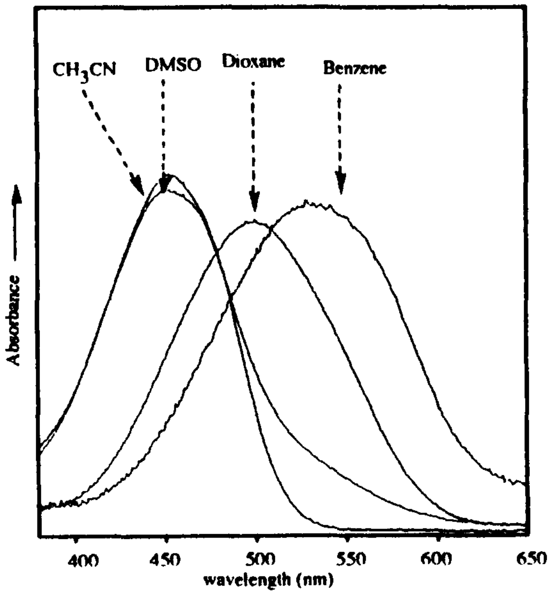
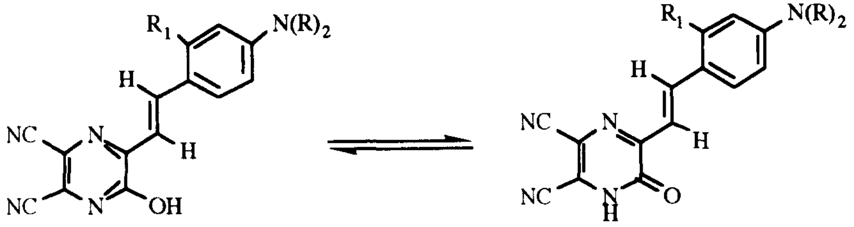


Fig. 2. Effect of polarity of solvent on λ_{max} of dye **4a**.



A
in polar medium

B
in non-polar medium

Scheme 3.

predominant in polar solvents, while tautomer **B** was predominant in non-polar solvents (Scheme 3). The PPP–MO calculation revealed that **A** absorbed at 452.0 nm and **B** absorbed at 504.7 nm. This supports the experimental results.

Molecular stacking effect

The absorption maxima of compounds **5–8** in solution and the solid state are summarized in Table 6. It is generally known that the λ_{max} of dyes in the solid state shift to longer wavelengths compared with those in solution because of the stronger molecular interactions of the dye molecules in the

TABLE 6
Difference in Absorption Maxima of Dyes between Solution and Solid State

Compound	λ_{max} *in* $CHCl_3$ *(nm)*	λ_{max} *in solid state (nm)*[a]	$\Delta\lambda$ *(nm)*[b]
5a	523	527	4
5b	543	540	−3
5c	531	540	9
6a	499	432	−67
6b	520	478	−42
6c	498	527	29
7a	499	432	−67
7b	523	608	85
7c	507	505	−2
8	425	423	2

[a] Vapour deposited thin film.
[b] $\Delta\lambda = \lambda_{solid} - \lambda_{solution}$.

solid state. The results, however, were quite different, and only dyes **7b** and **6c** showed $\Delta\lambda$ values of 85 nm and 29 nm, respectively. In contrast, dyes **6a**, **6b** and **7a** showed a large hypsochromic shift of λ_{max} in the solid state. The other dyes showed rather small $\Delta\lambda$ values and the λ_{max} of these dyes did not change significantly between the states. From these results, dye **7b** has a special molecular stacking in the solid state, a situation which is known in the case of some aminonaphthoquinone dyes and is caused by strong intermolecular π–π interactions.[9] The hypsochromic shift caused by dye aggregation is well known in cyanine dyes in which cancellation of the dipole moment is observed in the dimer. The styryl dyes synthesized have strong dipole moments even in the ground state, and a similar cancellation of the dipole moment is proposed for dyes **6a**, **6b** and **7a**.

The solid state structures of donor–acceptor chromophoric systems usually fall into one of two broad categories, as shown in Fig. 3: (1) those with all stacks in the same direction between donor (D) and acceptor (A) molecules; and (2) those with stacks in both directions between donor (D) and acceptor (A) molecules.

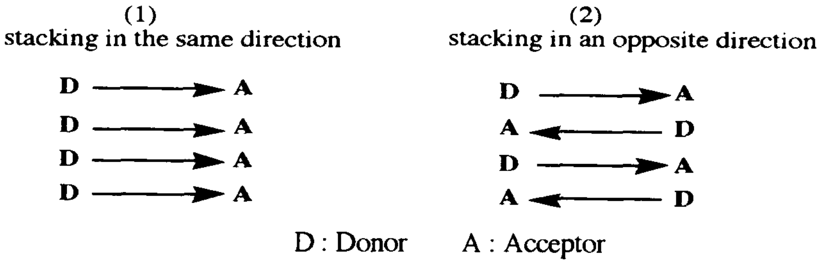


Fig. 3. Molecular stacking of styryl dyes.

The first structure is favourable to obtain a large dipole moment for nonlinear optical (NLO) materials. On the other hand, the dipole moment of the second structure will be cancelled completely. Therefore, the large difference ($\Delta\lambda$) for dye **7b** between solution and thin film, resulting from strong intermolecular interactions, seems apparently to reflect these facts. X-Ray crystal analysis of dye **7b** is being carried out and the results connected with NLO characteristics will be reported in due course.

EXPERIMENTAL

Identifications of compounds and measurements of properties were carried out by general procedures using the following equipment.

M.p.: Yanagimoto micro melting point apparatus, uncorrected.

NMR spectra: FT-NMR QE 300 MHz Shimadzu spectrometer, chemical shifts in ppm with reference to TMS.

Mass spectra (MS): M-80 B Hitachi mass spectrometer.

UV/vis spectra: U-3410 Hitachi spectrophotometer.

Fluorescence spectra: Shimadzu RF-5000 fluorescence spectrophotometer.

All chemicals were reagent grade and used without further purification unless otherwise specified. 2,3-Dicyano-5-methylpyrazine derivatives **3a–e**[9,10] and 4-diethylamino-2-methylbenzaldehyde[11] were prepared by known methods. 4-Dimethylaminobenzaldehyde and 4-diethylaminosalicylaldehyde were commercially available.

Syntheses of dyes 4–8

Method A: A solution of compound **3** (1 mmole) and arylaldehyde (1 mmole) in ethanol (10 ml) was refluxed in the presence of catalytic amounts of sodium ethoxide for 36 h. The solvent was partially removed *in vacuo*. The residue was poured into water, filtered, washed with water and dried. The product was submitted to column chromatography on silica gel.

Method B: A solution of compound **3** (1 mmole) and arylaldehyde (1 mmole) in Ac_2O (10 ml) was refluxed for 3–4 h. The solvent was removed *in vacuo*, and then the residue was treated as in Method A.

Method C: A solution of compound **5c** (1 mmole) in 1 N HCl (20 ml) was refluxed until the starting materials completely disappeared on TLC. The reaction mixture was cooled to room temperature and neutralized with 10% NaOH. The residue was poured into water, filtered, washed with water and dried. The crude product was submitted to column chromatography on silica gel with eluent.

Relevant data for the compounds are given below.

*2-[2-(4-Dimethylaminophenyl)ethenyl]-5,6-dicyano-3-hydroxypyrazine (**4a**)*

M.p.	< 300 °C
MS (m/z)	291 (M$^+$), 290 ((M−1)$^+$)
^{1}H-NMR (DMSO-D$_6$)	7.84–7.79 (d, 1H); 7.47–7.44 (d, 2H); 7.17–7.12 (d, 1H); 6.73–6.71 (d, 2H); 5.21 (s, 6H)
Eluent for column chromatography	CHCl$_3$/EtOH (10/1)

*2-[2-(4-Diethylamino-3-methylphenyl)ethenyl]-5,6-dicyano-3-hydroxypyrazine (**4b**)*

M.p.	< 300 °C
MS (m/z)	333 (M$^+$), 332 ((M−1)$^+$)
^{1}H-NMR (DMSO-D$_6$)	8.12–8.07 (d, 1H); 7.55–7.52 (d, 1H); 7.11–7.06 (d, 1H); 6.57–6.53 (d, 1H); 6.50 (s, 1H); 3.34–3.33 (q, 4H); 2.34 (s, 3H); 1.12–1.08 (t, 6H)
Eluent for column chromatography	CHCl$_3$/EtOH (10/1)

*2-[2-(4-Diethylamino-3-hydroylphenyl)ethenyl]-5,6-dicyano-3-hydroxypyrazine (**4c**)*

M.p.	< 300 °C
MS (m/z)	334 ((M−1)$^+$), 333 ((M−2)$^+$)
^{1}H-NMR (DMSO-D$_6$)	9.30 (s, 1H); 7.15–7.12 (d, 1H); 6.75–6.72 (d, 1H); 6.33–6.26 (d, 1H); 6.25–6.19 (d, 1H); 5.92 (s, 1H); 3.23–3.20 (q, 4H); 1.05–0.99 (t, 6H)
Eluent for column chromatography	CHCl$_3$/EtOH (10/1)

*2-[2-(4-Dimethylaminophenyl)ethenyl]-5,6-dicyano-3-acetoxypyrazine (**5a**)*

M.p.	< 300 °C
MS (m/z)	333 (M$^+$)
^{1}H-NMR (CDCl$_3$)	7.84–7.83 (d, 1H); 6.85–6.84 (d, 1H); 6.66–6.63 (d, 2H); 6.55–6.52 (d, 2H); 5.20 (s, 6H); 2.29 (s, 3H)
Eluent for column chromatography	EtOAc/n-hexane (2/3)

*2-[2-(4-Diethylamino-3-methylphenyl)ethenyl]-5,6-dicyano-3-acetoxypyrazine (**5b**)*

M.p.	218–220 °C
MS (m/z)	375 (M$^+$)

^{1}H-NMR (CDCl$_3$)	8.15–8.10 (d, 1H); 7.02–7.01 (d, 1H); 6.58–6.57 (d, 1H); 6.47–6.46 (d, 1H); 6.29 (s, 1H); 3.37–3.31 (q, 4H); 2.61 (s, 3H); 2.54 (s, 3H); 1.12–1.08 (t, 6H)
Eluent for column chromatography	EtOAc/n-hexane (1/3)

*2-[2-(4-Diethylamino-3-hydroylphenyl)ethenyl]-5,6-dicyano-3-acetoxypyrazine (**5c**)*

M.p.	236–237 °C
MS (m/z)	377 (M$^+$)
^{1}H-NMR (CDCl$_3$)	7.91–7.90 (d, 1H); 6.75–6.72 (d, 1H); 6.33–6.27 (d, 1H); 6.88–6.87 (d, 1H); 6.42–6.03 (m, 3H); 3.36–3.30 (q,4H); 2.47 (s, 3H); 1.15–1.11 (t, 6H)
Eluent for column chromatography	CHCl$_3$

*2-[2-(4-Dimethylaminophenyl)ethenyl]-5,6-dicyano-3-methylpyrazine (**6a**)*

M.p.	225 °C
MS (m/z)	289 (M$^+$)
H-NMR (DMSO-D$_6$)	8.10–8.05 (d, 1H); 7.56–7.53 (d, 2H); 6.95–6.90 (d, 1H); 6.72–6.69 (d, 2H); 3.08 (s, 6H); 2.72 (s, 3H)
Eluent for column chromatography	Et$_2$O

*2-[2-(4-Diethylamino-3-methylphenyl)ethenyl]-5,6-dicyano-3-methylpyrazine (**6b**)*

M.p.	235 °C
MS (m/z)	331 (M$^+$)
^{1}H-NMR (CDCl$_3$)	8.39–8.34 (d, 1H); 7.66–7.63 (d, 1H); 6.90–6.85 (d, 1H); 6.57–6.54 (d, 1H); 6.48 (s, 1H); 3.46–3.39 (q, 4H); 2.70 (s, 3H); 2.49 (s, 3H); 1.24–1.19 (t, 6H)
Eluent for column chromatography	EtOAc/n-hexane (1/1)

*2-[2-(4-Diethylamino-3-hydroylphenyl)ethenyl]-5,6-dicyano-3-methylpyrazine (**6c**)*

M.p.	232–234 °C
MS (m/z)	332 ((M$-$1)$^+$)
^{1}H-NMR (CDCl$_3$)	8.09–8.04 (d, 1H); 7.63–7.60 (d, 1H); 6.96–6.91 (d, 1H); 6.59–6.56 (d, 1H); 6.33 (s, 1H); 3.436–3.35 (q, 4H); 2.44 (s, 3H); 1.23–1.19 (t, 6H)
Eluent for column chromatography	CHCl$_3$

*2-[2-(4-Dimethylaminophenyl)ethenyl]-5,6-dicyanopyrazine (**7a**)*

M.p.	< 300 °C
MS (m/z)	275 (M^+)
^{1}H-NMR ($CDCl_3$)	8.64 (s, 1H); 7.98–7.93 (d, 1H); 7.55–7.52 (d, 2H); 6.91–6.86 (d, 1H); 6.72–6.69 (d, 2H); 3.08 (s, 6H)
Eluent for column chromatography	$CHCl_3$

*2-[2-(4-Diethylamino-3-methylphenyl)ethenyl]-5,6-dicyanopyrazine (**7b**)*

M.p.	221 °C
MS (m/z)	317 (M^+)
^{1}H-NMR ($CDCl_3$)	8.56 (s, 1H); 8.23–8.22 (d, 1H); 7.64–7.61 (d, 1H); 6.84–6.79 (d, 1H); 6.57–6.55 (d, 1H); 6.48 (s, 1H); 3.46–3.39 (q, 4H); 1.24–1.19 (t, 6H)
Eluent for column chromatography	$CHCl_3$

*2-[2-(4-Diethylamino-3-hyroxylphenyl)ethenyl]-5,6-dicyanopyrazine (**7c**)*

M.p.	240 °C
MS (m/z)	319 ($(M)^+$)
^{1}H-NMR ($DMSO\text{-}D_6$)	8.58 (s, 1H); 7.95–7.90 (d, 1H); 7.59–7.56 (d, 1H); 6.89–6.82 (d, 1H); 6.57–6.53 (d, 1H); 6.32 (s, 1H); 3.44–3.37 (q, 4H); 1.23–1.19 (t, 6H)
Eluent for column chromatography	$CHCl_3$/n-hexane (8/2)

*2-[2-(4-Diethylaminophenyl)ethenylcarboxylicacid]-5,6-dicyano-3-hydroxypyrazine (**8**)*

M.p.	243–245 °C
MS (m/z)	334 ($(M-1)^+$)
^{1}H-NMR ($CDCl_3$)	7.87 (s, 1H); 7.37 (d, 2H); 6.36 (d, 2H); 2.75 (s, 6H)
Eluent for column chromatography	EtOAc/n-hexane (8/2)

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