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Dyes and Pigments 40 (1998) 11–20

DYES AND PIGMENTS

Dicyanopyrazine Studies. Part V: Syntheses and Characteristics of Chalcone Analogues of Dicyanopyrazine

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Received 17 February 1998; accepted 19 March 1998

Abstract

Chalcone analogues based on 2,3-dicyanopyrazine were synthesized by the condensation reaction of 2-acetyl-methyl-5,6-dicyanopyrazine **4a** with various arylaldehydes. Oxidation of pentane-2,4-dione with selenium dioxide ga pentane-2,3,4-trione, which reacts with diaminomaleonitrile to give **4a**. These chalcolone dyes showed solvatochr mism depending on the polarity of the solvents, but the chromophoric system was interupted at the carbonyl group steric requirements of substituents. The seven membered azepine, obtained from diaminomaleonitrile and a 1,3-dica bonyl compound, was further reacted with an arylaldehyde to give a new fluorescent heterocycle. Optimization of t chemical structure of the products was evaluated by the MOPAC PM 3 method and was correlated with their spectr properties. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Dicyanopyrazine; Chalcone; Azepine; Nonlinear optics; MOPAC; Solvatochromism

1. Introduction

Chalcones are of potential interest in the context of second harmonic generation material in nonlinear optics [1,2]. 2,3-Dicyanopyrazines are very powerful electron acceptors, and are especially suitable building blocks for the strong intramolecular charge-transfer chromophoric system which is necessary for 2nd order nonlinear optical materials. We have previously reported the possible application of the pyrazine chromophore for use in a variety of functional dye materials [3,4]. In particular, dicyanopyrazines can be used as a convenient precursor for fluorescent dyes, and ca be applied as an emitter for electroluminescen devices [5]. We have been interested in the chem cal, electronic and physical properties of dicy nopyrazine oriented dyes, with the intention introducing new functionalities into these dono acceptor chromophoric systems [6]. The propos dyes have a strong intramolecular charge-transf character and have an ability to give strong inte molecular π–π interactions for molecular stackin and thus have large dipole moments in the excit state, giving large dipole moment differences laser irradiation. These problems are very impo tant for nonlinear optical materials [7].

In previous papers [8,9], we reported t syntheses and properties of dicyanopyrazi oriented styryl type dyes. We evaluated the

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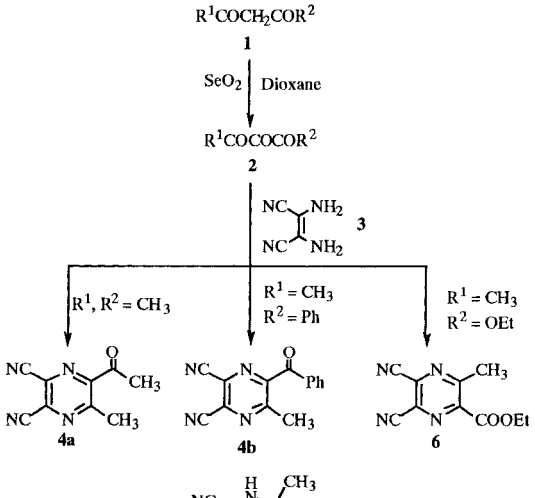
PII: S0143-7208(98)00023-0



Scheme 1.

absorption spectra by using the Pariser–Parr–Pople molecular orbital calculation method, and optimization of their structures was performed by using the MOPAC with the PM 3 method [10]. These methodologies are very valuable for the design, synthesis and correlation of chemical structures with physical properties.

In this paper, we report the synthesis of some dicyanopyrazine oriented chalcone dyes and styryl fluorescent dyes, and evaluate their absorption spectra with respect to substituent effect. A new 7-membered diazepine derivative, obtained from the reaction of a 1,3-dicarbonyl compound with diaminomaleonitrile, was developed to synthesize new heterocycles.

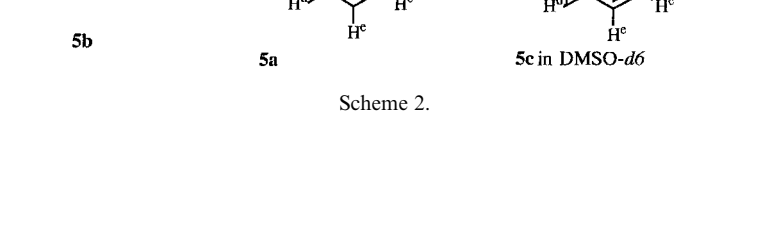
2. Results and discussion

2.1. Condensation reaction of 4 with aryl aldehydes

The classical synthesis of 5,6-dicyanopyrazin involves the condensation of diaminomaleonitrile and 1,2-dicarbonyl compound. The reaction is fac and has been widely used for the synthesis of 5, dicyanopyrazine derivatives [3].

Selective oxidation of the 1,3-dicarbonyl com pounds [**1**] by selenium oxide gave the corr sponding 1,2,3-tricarbonyl compound [**2**], such the acetyl or benzoyl derivatives of the 1,2-dica bonyl compound. Condensation of diaminomale nitrile **3** with 1,2,3-tricarbonyl compound deriv from acetylacetone gave 2-acetyl-3-methyl-5, dicyanopyrazine **4a** in 22% yield. However, t reaction of **3** with 1-phenyl-1,3-butanedione pr viously treated with selenium dioxide gave 2-be zoyl-3-methyl-5,6-dicyanopyrazine **4b**, togeth with the 7-membered azepine **5** (2,3-dicyano- hydroxy-7-phenyl-5-methyl-1,4-diazacycloheptı 2,5-diene) in 19% and 8% yields, respectivel Compound **5** was obtained from the reaction of with **1** ($R^1=CH_3$ $R^2=Ph$). 2-Carboxyethyl- methyl-5,6-dicyanopyrazine **6** was obtained wh ethylacetoacetate as a starting material was pr viously treated with selenium dioxide and react with **3**. The results are summarized in Scheme 1.

On the other hand, compound **5** has an acti methylene group and exists predominantly as t tautomeric structure **5a** in the solid state and fresh solution (Scheme 2). The IR spectrum of indicates separated peaks at around 3300 cm^{-1} f two of the NH stretching absorption, and anoth peak at 3500 cm^{-1} for the OH stretching absorptio The ^{1}HNMR spectra of **5** indicate an equilibriu



Scheme 2.

mixture of **5a** and the deprotonated form in DMSO-d_6. In chloroform-*d*, only **5a** was detected as a single species (Fig. 1(a)), but in DMSO-d_6, two sets of signals were observed (Fig. 1(b)). Their ratio was 0.84 for **5a** and 0.16 for the deprotonated species, from the integral value of the 5-methyl signal. On addition of D_2O to the DMSO d_6, solution, the signals for OH and NH di appeared (Fig. 1(c)). From these observations, in DMSO exists as a mixture of **5a** and t deprotonated species **5c** which is stabilized DMSO. The NH signals of **5a** in DMSO-d_6 we

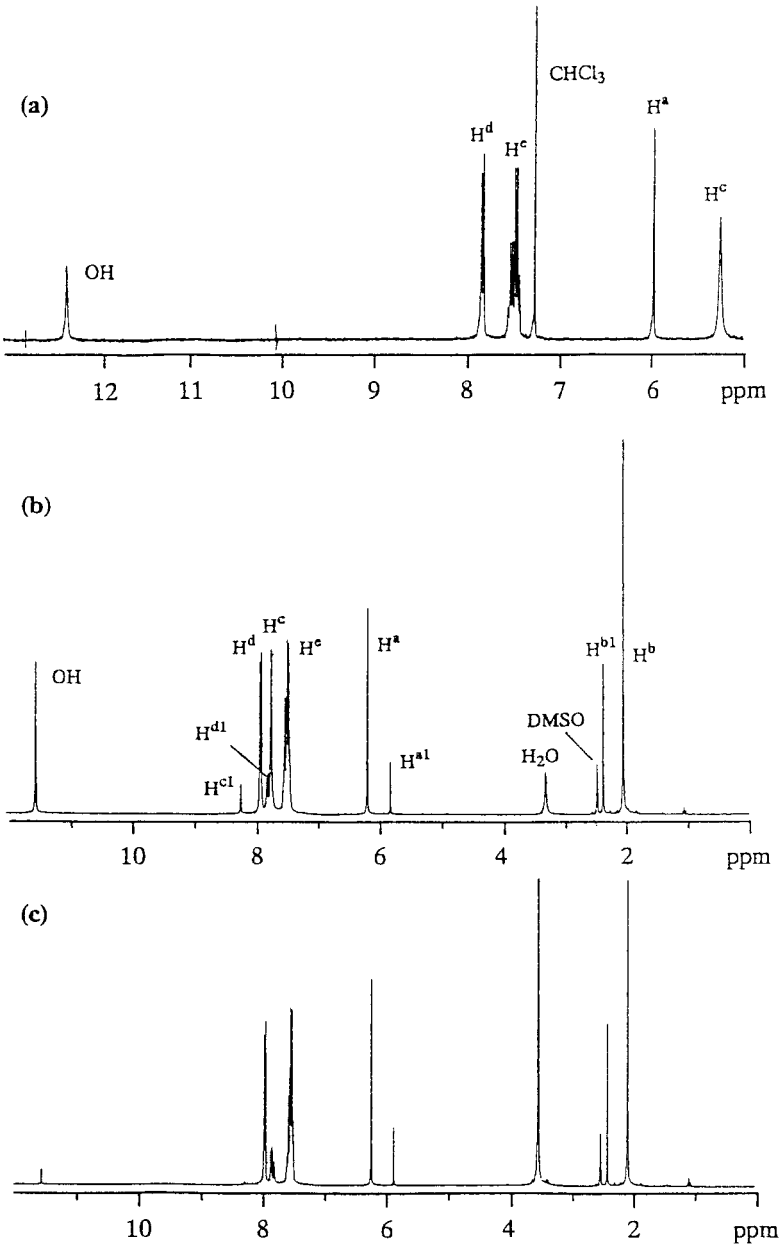


Fig. 1. 300 MHz ^{1}H-NMR Spectra of 5; (a) in $CDCl_3$, (b) in DMSO-d_6, (c) addition of D_2O to (b).

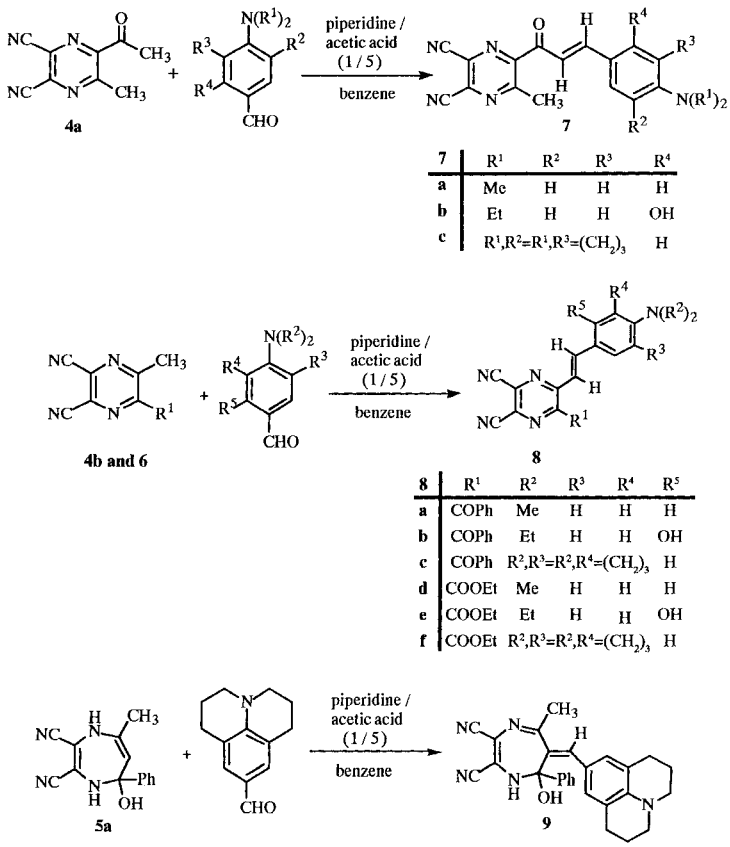
observed downfield compared with these in chloroform-*d* because of the intermolecular hydrogen bonding with the oxygen atom of DMSO. The contribution of **5b** was negligible as evidence from the NMR spectra of **5**. The Chalcone derivatives **7** are easily synthesized by the Knoevenagel condensation of **4a** and arylaldehydes in the presence of piperidine and acetic acid (1:5) as catalyst. Similar reaction of **4b** or **6** with arylaldehydes gave styryldicyanopyrazine dyes **8**. However, the reaction of **5** with 4-julolidinylaldehyde under the same reaction conditions gave the undesired 6-(4-julolidinyimethylene)-2,3-dicyano-5-methyl-7-hydroxy-7-phenyl-1,4-diazacyclohepta-2,4-diene **9**. The formation of **9** resulted from nucleophilic attack of the enamine moiety of **5a** to the aldehyde carbonyl, and the structure of **5a** was thus confirmed by this reaction. Results are summarized in Scheme 3 and Table 1.

2.2. Visible spectra

Visible spectra in solution and solvent effec
are summarized in Table 2. The absorption ma
imum of **7–9** in chloroform showed bathochrom

Table 1
Condensation reaction of **4–6** with arylaedehydes

Run	Reactant	Time(hr)	Product	Yield (%)
1	**4a**	16	**7a**	48
2	**4a**	10	**7b**	63
3	**4a**	12	**7c**	67
4	**4b**	9	**8a**	83
5	**4b**	9	**8b**	80
6	**4b**	15	**8c**	36
7	**6**	8	**8d**	67
8	**6**	8	**8e**	70
9	**6**	8	**8f**	74
10	**5a**	14	**9**	41



Scheme 3.

shifts of 10–20 nm compared with those in benzene, but in general there were only limited solvent effects depending on the solvent polarity. The chromophoric system of the chalcone derivative has been evaluated by the PPP MO method [1 the two aromatic rings were not coplanar ar their observed λ max were at much shorter wav length than those of the calculated values. T

Table 2
Solvent effects on visible spectra of dyes **7–9**

Comp	Benzene (nm)	$CHCl_3$(nm)[logε]	EtOAc (nm)	CH_3OH (nm)	DMSO (nm)
7a	523	534 [4.79]	506	507	526
7b	532	550 [4.79]	534	540	550
7c	565	579 [4.80]	551	562	578
8a	513	526 [4.70]	500	504	517
8b	516	534 [4.72]	515	534	543
8c	558	575 [4.72]	556	551	561
8d	511	526 [4.67]	498	499	514
8e	519	539 [4.73]	521	529	539
8f	553	572 [4.74]	542	548	559
9	546	554 [4.50]	541	547	561

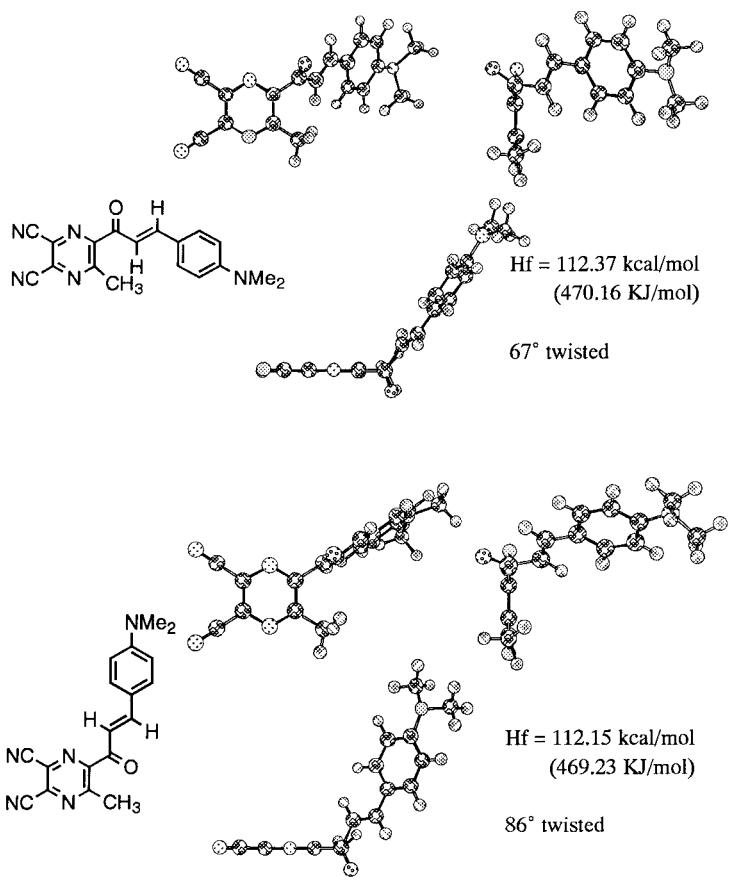


Fig. 2. Optimized structure of **7a** by the MOPAC PM3 method.

PPP MO calculation was conducted for a planar structure. Structural optimization of **7** was conducted by the MOPAC PM 3 method, which reveal a non-planar structure (Fig. 2). The two optimized structures of **7a** were twisted 67° or 86° at the carbonyl unit, respectively, and therefore through conjugation from the aniline to the pyrazine moiety cannot be considered.

The λ max of dyes **7** is related to the intramolecular charge-transfer chromophoric system in which the aniline moiety acts as donor and the carbonyl group as an acceptor; and then λ max thus undergoes bathochromic shifts depending on the order of electron donating ability of the donor moiety (**7a**→**7c**).

In the case of the styryldicyanopyrazines **8**, their basic chromophoric system have been already evaluated [4] and an intramolecular charge-transfer chromophoric system in planar situation was confirmed by the MOPAC PM 3 method [5]. The substituent effects of dye **8** were also understandable on the basis of a donor-acceptor system. As a result, dyes **7c** and **8c**, which have the same donor moiety, absorbed in the same wavelen region (Fig. 3). The absorption spectra of showed two peaks at 381 and 554 nm. The λ m at 381 nm is attributed to the azepine chrom phore (**5a** absorbs at 375 nm in benzene), and t λ max at 554 nm is attributed to the throu conjugated π-system. Structural optimization o by MOPAC PM 3 method revealed the nonplan structure of **9** was evaluated (Fig. 4). The plan julolidine moiety was not as highly conjugat with the azepine moiety in each of the optimiz structures. This resulted in the nonplanar structu of 2,3-dicyano-5-methyl-6-methylene-7-hydroxy- phenyl-1,4-diazacyclohepta-2,4-diene **10** in whi the external conjugated ethylene unit was d torted 63° for **10a** or 56° for **10b** from the azepi moiety. Dye **9** showed red fluorescence at 610 n and is therefore a potentially interesting ne fluorescent chromophore.

On the other hand, dye **9** showed reversib absorption spectra changes depending on t photo-irradiation. Irradiation at 540 nm of dye in benzene produced a hypsochromic shift of t

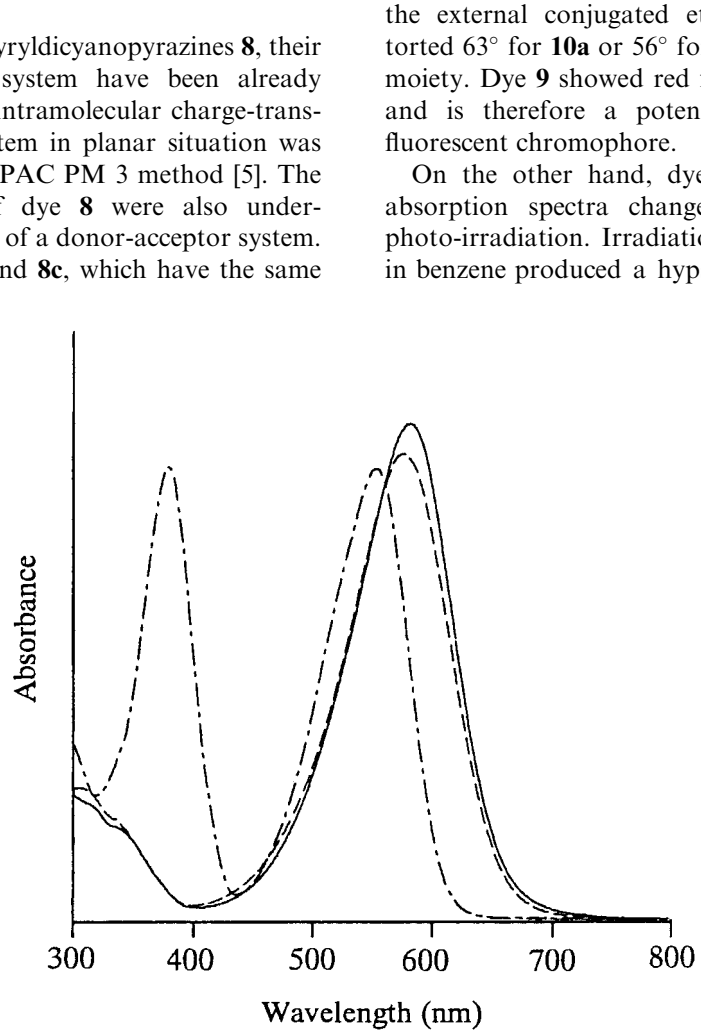


Fig. 3. Absorption spectra of **7c** (—), **8e** (- - -) and **9** (–·–) in chloroform.

long-wavelength absorption band from 546 to 527 nm, accompanied by an increase of absorbance from 33,400 to 43,500 during 10 min. This was resulted from the much more planar π-conjugation after irradiation than the twisted π-conjugation before irradiation (Fig. 5). The reverse process was also observed when UV light at 370 nm was irradiated. This phenomena may be due to photo induced structure isomerization of the azepine moiety. Structural analysis of photo-

isomerization product is being investigated ar
the results will be reported in due course.

3. Experimental

3.1. General

Melting points were determined on a Yanagimo
micro melting point aparatus without correctio

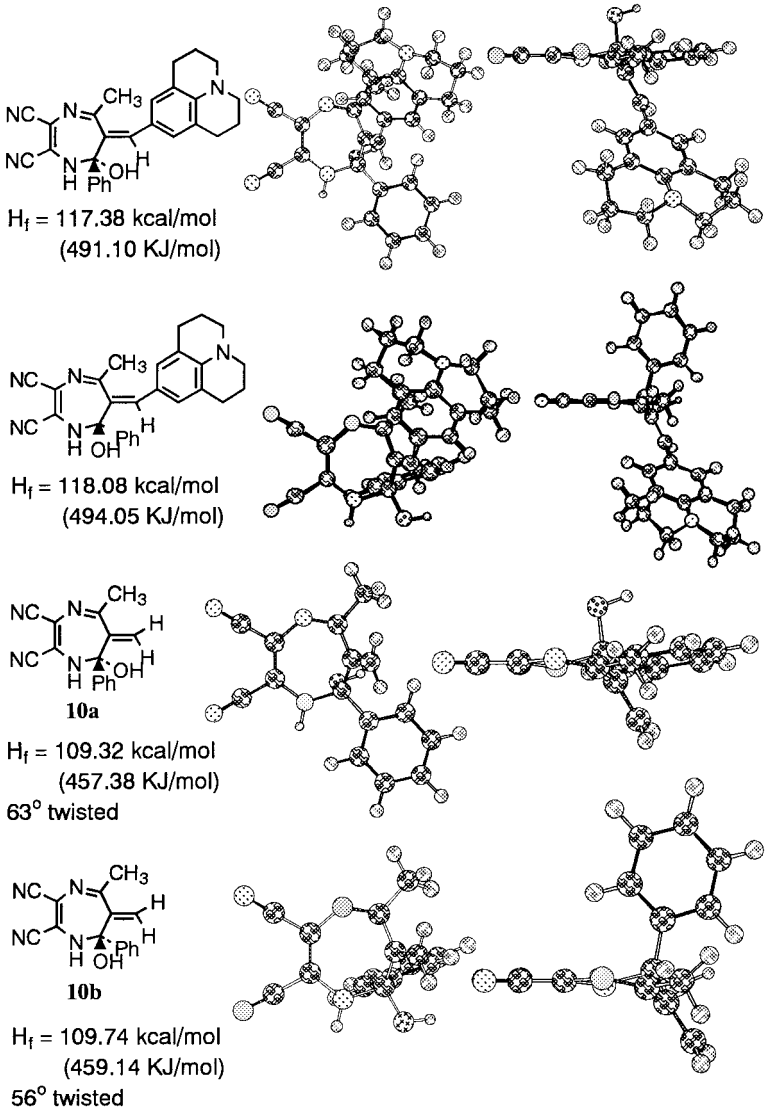


Fig. 4. Optimized structures of **9** and **10** by the MOPAC PM3 method.

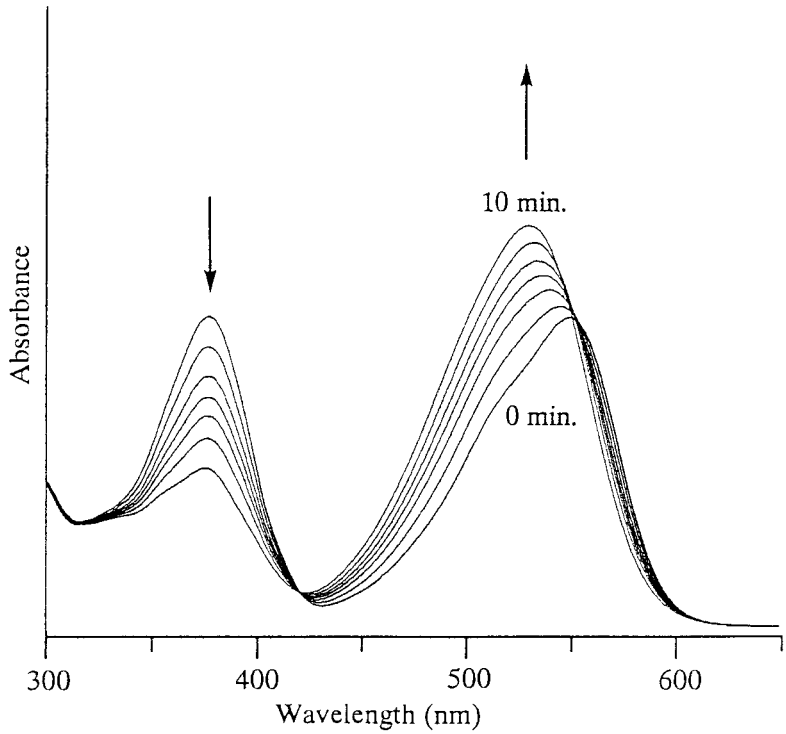


Fig. 5. Spectral changes of **9** in benzene (5.2×10^{-6} mol/1) irradiated at 540 nm for 10 min.

The ^{1}HNMR spectra were taken on an FT-NMR θE 300 MHz Shimadzu spectrometer; mass spectra were recorded on M-80 B Hitachi and Shimadzu GCM S-θP 5000 mass spectrometers. The visible and fluorescence spectra were measured on a U-3410 Hitachi spectrophotometer and a Shimadzu RF-5000 fluorescence spectrophotometer respectively. Microanalysis was conducted using a Yanaco CHN MT-3 recorder. All chemicals were of reagent grade and were used without further purification unless otherwise specified.

3.2. Syntheses of **4**, **5** and **6**

A mixture of dioxane (25 ml), water (1 ml), selenium dioxide (5.55 g, 50 mmol) and **1** (50 mmol) was refluxed for 8 h. Residual selenium was filtered off and washed with dioxane (5 ml). To the resulted solution was added diaminomaleonitrile **3** (5.40g, 50 mmoles), and the mixture then was refluxed for 2 h, after which the solvent was evaporated under reduced pressure. The residue was extracted with chloroform (100 ml) and the extra concentrated under reduced pressure. The cru product was purified by column chromatograp on silica gel using chloroform as eluent.

3.2.1. 2-Acetyl-3-methyl-5,6-dicyanopyrazine (**4a**

The crude product was recrystallized from ca bon tetrachloride to give **4a** in 22% yield as whi needles, mp 92–93°C; ms: m/z 186 (M^+); ^{1}H NM ($CDCl_3$): δ 2.96 (s,3H,$COCH_3$), 2.75(s,3H,CH Anal. calc. for $C_9H_6N_4O$: C, 58.06; H, 3.25; 30.10. Found: C, 57.68; H, 3.25; N, 29.96.

3.2.2. 2-Benzoyl-3-methyl-5,6-dicyanopyrazine (**4**

The crude product was recrystallized from eth to give **4b** in 19% yield as a pale yellow solid, m 117–118°C; ms: m/z 248(M^+); ^{1}H NMR (CDCl δ 7.82 (2H, d, J 7.2, phenyl protons), 7.72 (1H, t 7.2, phenyl proton), 7.55 (2H, t,J 7.2, phenyl pr tons), 2.78(3H, s, CH_3). Anal. calc. for C H_8N_4O: C, 67.74; H, 3.25; N, 22.57. Found: 68.07; H, 3.21; N, 22.61.

*3.2.3. 2,3-Dicyano-5-methyl-7-hydroxy-7-phenyl-1,4-diazacyclohepta-2,5-diene (**5**)*

The crude product was recrystallized from ether to give **5a** in 8% yield as a yellow solid, mp 173–174°C; ms: *m/z* 252 (M^+); ^{1}H NMR ($CDCI_3$): ·δ 12.26(br. s, 1H, OH), 7.83 ((d + d), 2H, phenyl protons), 7.47 (m, 3H, phenyl protons), 5.95(s, 1H, CH), 5.23(br.s, 2H, NH), 2.07(s, 3H, CH_3). Anal. calc. for $C_{14}H_{12}N_4O$: C, 66.66; H, 4.79; N, 22.21. Found: C, 66.59 ; H, 4.78; N, 22.09.

*3.2.4. 2-Carboxyethyl-3-methyl-5,6-dicyanopyrazine (**6**)*

The crude product was recrystallized from ethanol to give **6** in 15% yield as white needles, mp 153–154°C; ms: m/z 216 (M^+); ^{1}H NMR ($CDC1_3$): δ 7.13 (2H, q, *J* 7.2, CH_2), 2.05 (3H, s, CH_3), 1.27(3H, t, *J* 7.2, CH_2CH_3). Anal. calc. for $C_{10}H_8N_4O_2$. C, 55.56; H, 3.73; N, 25.92. Found: C, 54.82; H, 3.61; N, 25.41.

*3.3. Syntheses of 7–**9***

The appropriate Dicyanopyrazines (**4**–**6**, 5 mmol) and arylaldehydes (**6a**–**6c**, 5 mmol), two drops of piperidine/acetic acid (v/v = 1/5) were dissolved in dry benzene (30 ml) and the mixtures heated under on a Dean and Stark water trap for 18 h and then cooled to room temperature. The resulting precipitates were filtered, washed with benzene and dried, to give the crude products.

*3.3.1. 2-[3-(4-N,N-dimethylaminophenyl)acryloyl]-3-methyl-5,6-dicyanopyrazine (**7a**)*

The crude product was purified by column chromatography on silica gel using benzene as eluent. Compound **7a** was obtained as red crystals, mp 234–235°C; *m/z* 317 (M^+); ^{1}H NMR ($CDCI_3$) δ 2.73 (3H, s,CH_3) 3.09 (6H, s, $N(CH_3)_2$), 6.69 (2H, d, *J* 9.0, ArH), 7.75 (2H, d, *J* 9.0, ArH), 7.81 (1H, d, *J* 15.3, CH = C*H*-Ar), 8.23 (IH, d,*J* 15.3, CH = C*H*-Ar). Anal. calc. for $C_{18}H_{15}N_5O$: C, 68.13; H, 4.76; N, 22.07. Found: C, 67.66 ; H, 4.56; N, 21.56.

*3.3.2. 2-[3-(4-N,N-diethylamino-3-hydroxyphenyl)-acryloyl]-3-methyl-5,6-dicyanopyrazine (**7b**)*

The crude product was purified by column chromatography on silica gel using ethylacetate as eluent. Compound **7b** was obtained as red crysta mp 205–207°C; *m/z* 360 (M^+-1); ^{1}H NM ($CDC1_3$) δ 1.22 (6H, t, *J* 6.9, CH_2CH_3), 2.70 (3 s,CH_3), 3.42 (4H, q, *J* 6.9, CH_2CH_3), 6.01 (1H, ArH), 6.32 (1H, d, *J* 9.3, ArH), 7.48 (1H, d, *J* 9. ArH), 7.86 (1H, d, *J* 15.0, CH = *CH*-Ar), 8.47 (1 d, *J* 15.0, CH = *CH*Ar). Anal. calc. f $C_{20}H_{19}N_5O_2$: C, 66.47; H, 5.30; N, 19.38. Foun C, 65.92; H, 5.14; N, 18.71.

*3.3.3. 2-[3-(4-Julolidinyl)acryloyl]-3-methyl-5,6-di-cyanopyrazine (**7c**)*

The crude product was recrystallized fro ethanol to give **7c** as dark blue crysta mp > 300°C; *m/z* 369 (M^+); ^{1}H NMR ($CDC1_3$) 1.96 (4H, t, *J* 6.3, CH_2), 2.71 (3H, s,CH_3), 2. (4H, t, *J* 6.3, $ArCH_2$) , 3.31 (4H, t, *J* 6.3, CH 7.16 (2H, s, ArH), 7.66 (1H, d, *J* 15.3, CH = C Ar), 8.06 (1H, d, *J* 15.3, CH = C*H*-Ar). Anal. ca for $C_{22}H_{19}N_5O_1$: C, 71.53; H, 5.18; N, 18.9 Found: C, 71.47; H, 4.49; N, 18.20.

*3.3.4. 2-[2-(4-N,N-dimethylaminophenyl)ethenyl 3-benzoyl-5,6-dicyanopyrazine (**8a**)*

The crude product was recrystallized from eth nol to give **8a** as dark red crystals, mp 255–254 ° *m/z* 379 (M^+); ^{1}H NMR ($CDC1_3$) δ 3.06 (6H, $N(CH_3)_2$), 6.66 (2H, d, *J* 9.0, ArH), 6.96 (1H, d, 15.3, CH = C*H*-Ar), 7.49 (2H, d, *J* 9.0, ArH), 7. (2H, t, *J* 7.8, ArH), 7.73 (1H, t, *J* 7.8, ArH), 7. (2H, d, *J* 7.8, ArH), 8.21 (1H, d, *J* 15.3, C*H* = C Ar). Anal. calc. for $C_{23}H_{17}N_5O$: C, 72.81; H, 4.5 N, 18.46. Found: C, 71.99; H, 4.63; N, 18.35.

*3.3.5. 2-[2-(4-N,N-diethylamino-3-hydroxyphenyl ethenyl]-3-benzoyl-5,6-dicyanopyrazine (**8b**)*

The crude product was purified by colun chromatography on silica gel using chloroform eluent . Compound **8b** was obtained as blue cry tals, mp 236–237°C; *m/z* 422 (M^+-1); ^{1}H NM ($CDC1_3$) δ 1.19 (6H, t, *J* 6.9, CH_2CH_3), 3.38 (4 q, *J* 6.9, CH_2CH_3), 5.95 (1H, s, ArH), 6.28 (1H, *J* 9.0, ArH), 7.06 (1H, d, *J* 15.0, C*H* = CH Ar),7.36(1H,d,*J*9.0,ArH), 7.53 (2H,t,*J*7.8,ArH 7.68 (1H,d,*J* 7.8,ArH), 7.88 (2H,d,*J* 7.8,ArH 8.43 (1H,d,*J* 15.0,C*H* = CH-Ar). Anal. calc. f $C_{25}H_{21}N_5O_2$: C, 70.91; H, 5.00; N, 16.54. Foun C, 70.41 ; H, 4.92; N, 16.46.

*3.3.6. 2-[2-(4-Julolidinyl)ethenyl]-3-benzoyl-5,6-dicyanopyrazine (**8c**)*

The crude product was recrystallized from ethanol to give **5c** as dark blue crystals, mp 287–288 °C; *m/z* 431 (M^+); ^{1}H NMR ($CDCI_3$) δ 1.95 (4H, t, *J* 6.0, CH_2), 2.72 (4H, t, *J* 6.0, $ArCH_2$), 3.31 (4H, t, *J* 6.0, NCH_2), 6.85 (1H, d, *J* 15.0, CH=C*H*-Ar), 7.02 (2H, s, ArH), 7.56 (2H, t, *J* 7.8, ArH), 7.72 (1H, t, *J* 7.8, ArH), 7.89 (2H, d, *J* 7.8, ArH),8.08(1H, d, *J* 15.0, C*H*=CH-Ar). Anal. calc. for $C_{27}H_{21}N_5O_1$: C, 75.16; H, 4.91; N, 16.23. Found: C, 75.56; H, 5.15; N, 15.83.

*3.3.7. 2-[2-(4-N,N-dimethylaminophenyl)ethenyl]-3-carboxyethyl-5,6-dicyanopyrazine (**8d**)*

The crude product was recrystallized from ethanol to give **8d** as dark red crystals, mp 172–173°C; *m/z* 347 (M^+); ^{1}H NMR ($CDC1_3$) δ 1.48 (3H, t, *J* 6.9, CH_2 CH_3), 3.10 (6H, s, $N(CH_3)_2$), 4.52 (2H, q, *J* 6.9, CH_2CH_3), 6.65 (2H, d, *J* 9.0, ArH), 7.53 (1H, d, *J* 15.3, CH=C*H*-Ar), 7.57 (2H, d, *J* 9.0, ArH), 8.20 (1H d, *J* 15.3, C*H*=CH-Ar). Anal. calc. for $C_{19}H_{17}N_5O_2$: C, 65.70; H, 4.93; N, 20.16. Found: C, 65.05 ; H, 4.92; N, 20.16.

*3.3.8. 2-[2-(4-N,N-diethylamino-3-hydroxyphenyl)-ethenyl]-3-carboxyethyl-5,6-dicyanopyrazine (**8e**)*

The crude product was purified by column chromatography on silica gel using benzene/ ethylacetate (10/1) as eluent. Compound **8e** was obtained as blue crystals, mp 139–140°C; *m/z* 390 (M^+-1); ^{1}H NMR ($CDCI_3$) δ 1.19 (6H, t, *J* 6.9, NCH_2CH_3), 1.47 (3H, t, *J* 6.9, OCH_2CH_3), 3.39 (4H, q, *J* 6.9, NCH_2CH_3), 4.52 (2H, q, *J* 6.9, OCH_2CH_3), 6.01 (1H, s, ArH), 6.31 (1H, d, *J* 9.0, ArH), 7.46 (1H, d, *J* 9.0, ArH), 7.59 (1H, d, *J* 15.0, CH=C*H*-Ar),8.42 (1H, d, *J* 15.0, CH=C*H*-Ar). Anal. calc. for $C_{21}H_{21}N_5O_3$: C 64.44; H, 5.41; N, 17.89. Found: C, 63.70 ; H, 5.18; N, 17.62.

*3.3.9. 2-[2-(4-Julolidinyl)ethenyl]-3-carboxyethyl-5,6-dicyanopyrazine (**8f**)*

The crude product was recrystallized from ethanol to give **8f** as dark blue crystals, mp 270–271°C; *m/z* 399 (M^+); ^{1}H NMR ($CDCI_3$) δ 1.46 (3H, t, *J* 6.9, OCH_2CH_3), 1.97 (4H, t, *J* 6.0, CH_2), 2.76 (4H, t, *J* 6.0, $ArCH_2$), 3.34 (4H, t, *J* 6.0, NCH_2), 4.54 (2H, q, *J* 6.9, OCH_2CH_3), 7.10 (2H, s, ArH), 7.40 (1H, d, *J* 15.0, CH=C*H*-Ar), 8.08 (1H, d, *J* 15.
C*H*=CH-Ar). Anal. calc. for $C_{23}H_{21}N_5O_2$:
69.16; H, 5.30; N, 17.53. Found: C, 68.40; H, 5.1
N, 17.16.

*3.3.10. 6-[2-(4-Julolidinyl)ethenyl]-2,3-dicyano-7-hydroxy-7-phenyl-5 -methyl-1,4-diazacyclohepta-2,diene (**9**)*

The crude product was recrystallized fro
ethanol to give **9** as dark brown crystals, mp 26
265°C; *m/z* 435 (M^+); ^{1}H NMR ($CDCl_3$) δ 1.
(4H, t, *J* 5.4, CH_2), 2.51 (3H, s, CH_3), 2.84 (4
br.t, *J* 5.4, $ArCH_2$), 3.34 (4H, t, *J* 5.4, NCH_2), 6.
(1H, s, =CH-Ar), 7.36(2H, s, ArH), 7.45 (3H, t,
7.5, ArH), 7.96 (2H, d, *J* 7.5, ArH), 8.26 (1H,
NH), 14.06 (1H, br. s, OH). Anal. calc. f
$C_{27}H_{25}N_5O_1$: C, 74.46; H, 5.79; N, 16.08. Foun
C, 74.22; H, 5.57; N, 15.89.

Acknowledgements

The MOPAC calculations were carried out
Miss K. Shirai in KIT. DAMN was supplied
Nippon Soda Co. Ltd. The authors are great
indebted to them.

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