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Syntheses and spectral properties of non-planar bis(styryl)diazepine fluorescent dyes and related derivatives

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Abstract

New bis(styryl)dicyanodiazepine fluorescent dyes and related derivatives were synthesized by the condensation of 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine and related compounds with arylaldehydes. Their optimized molecular structures were evaluated by the MOPAC PM3 method and MO calculations were conducted by means of the ZINDO method. The bis(styryl) dye showed very broad visible absorption spectra with triple absorption maxima which can be considered to arise from splitting of the degenerate HOMO's. The effects of ring size and substituents on the absorption and fluorescence spectra of a series of new styryldiazepine dyes have been interpreted in terms of the non-planar diazepine component of the chromophoric system. The strong intramolecular charge transfer chromophoric system of these dyes exhibited an exceptionally large Stokes shift of more than 100 nm, which resulted in pure red fluorescence at wavelengths beyond 600 nm.

Keywords: 2,3-Dicyano-5,7-dimethyl-6*H*-1,4-diazepine; Bis(styryl)diazepine fluorescent dye; Non-planar fluorescent chromophore; MOPAC PM3; ZINDO calculation; Red EL emitter

1. Introduction

Fluorescent chromophores have been generally known to have a planar and rigid π-conjugation system, and many well known fluorescent chromophores have rigid ring systems such as stilbene, coumarin, naphthalimide, perylene and rhodamine. We have developed new fluorescent chromophores based on pyrazine nucleus and reported many new fluorescent dyes [1]. Organic fluorescent materials are currently under investigation for various application fields such as emitters for electroluminescence (EL) devices and copy-preventing inks. In particular, fluorescent dye materials which emit red fluorescence are desirable for use in full color EL display [2].

In the previous paper [3], we reported syntheses of new styryldiazepine fluorescent dyes and their spectral properties were correlated with their non-planar molecular structures.

In this paper, we describe the synthesis of a series of new styryldicyanodiazepine fluorescent dyes by the condensation of methyl-2,3-dicyano-6*H*-1,4-diazepine and related intermediates with aryl aldehydes. Their absorption and fluorescent spectral properties were correlated with their non-planar

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molecular structure. Their optimized molecular structures were evaluated by the MOPAC PM3 method and MO calculations were conducted by means of the ZINDO method [4]. It is known that 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine can be synthesized from pentane-1,3-dione and diaminomaleonitrile [5]. 1,4-Diazepine has a seven-membered ring and has a non-planar, non-conjugated ring system at the 6-methylene group. Structural and substituent effects of styryldiazepine dyes on their absorption and fluorescent spectra in solution were correlated with their chromophoric systems with regard to the non-planar diazepine moiety.

2. Results and discussion

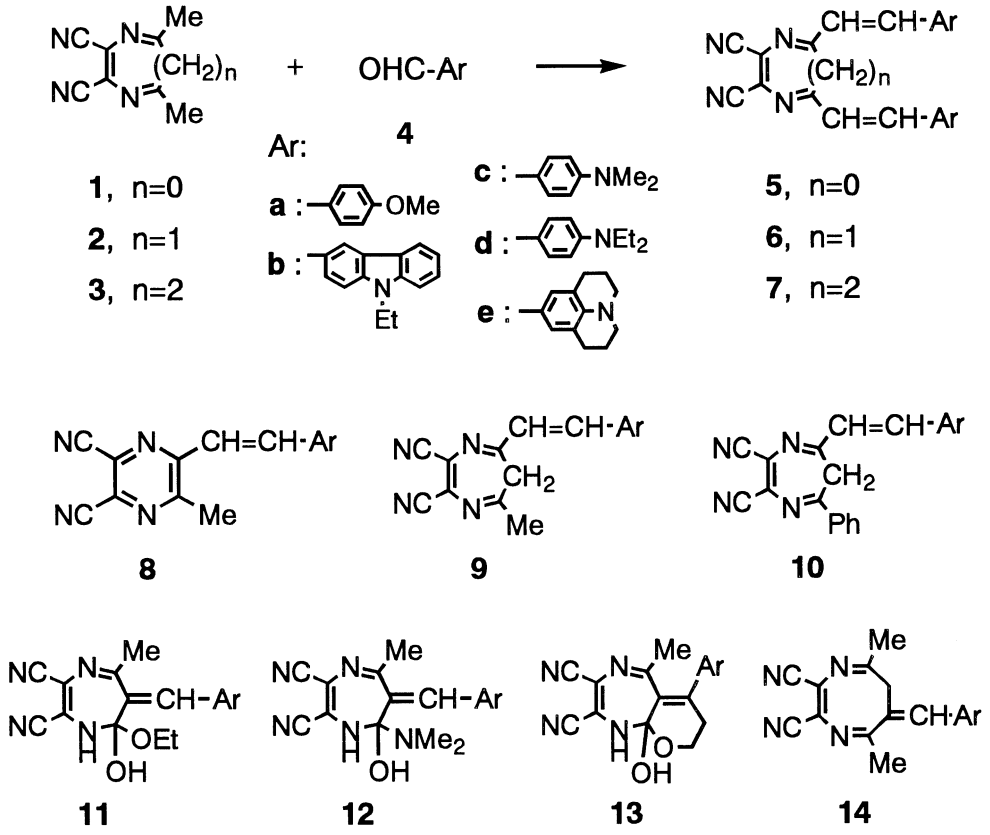
2.1. Syntheses of new bis(styryl)dicyanodiazepine and related fluorescent dyes

The methyl groups attached to the dicyanopyrazine or dicyanodiazepine rings are acidic and are reactive towards carbonyl groups under basic conditions [3,6]. Three types of dicyanopyrazine analogues, 2,3-dicyano-5,6-dimethylpyrazine (**1**), 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (**2**) and 2,3-dicyano-5,8-dimethyl-1,4-diazacyclooctane-2,4,6-triene (**3**) were synthesized by the condensation reaction of diaminomaleonitrile (DAMN) with the corresponding diketones. They have ring sizes of six (**1**), seven (**2**) and eight (**3**), and the planar structure is anticipated for **1** but the other two have non-planar structures. Their non-planar molecular structures were evaluated by computational chemistry by using the ab initio [7] and MOPAC PM3 methods. The reactions of **1**–**3** with arylaldehydes (**4**) in benzene were conducted in the presence of piperidine to synthesize **5**–**7**, respectively. But, while the corresponding **5** and **7** were not obtained in the cases of **1** and **3**, the corresponding monostyryl derivatives **8** and **14** were obtained, respectively. The synthesis of **5c** was conducted by using the Wittig reaction [8], and the second methyl group of **8** has no more reactivity toward aryl carbonyl group to give **5**. In the case of **2**, bis(styryl) derivatives with different substituents (**6a**–**6e**) were obtained together with the monostyryl derivatives **9**. Reactions of azepines with arylaldehydes having different electron-donating substituents are summarized in Scheme 1. The structures of styryldiazepine derivatives are also shown in Scheme 1. General synthetic methods were reported in our previous paper [3].

*2.2. Optimized molecular structure of **3** by the ab initio calculation method*

The optimized molecular structure of **2** was evaluated by the ab initio method and the molecular structure was found to deviate from planarity at the 6-methylene group [3]. These observations were also confirmed by the geminal coupling of the 6-methylene protons by ^{1}H-NMR spectra [3]. On the other hand, the methyl groups at the 5- and 8-positions of **3** are observed at 2.13 ppm (6H) as singlet, and the two methylene groups at the 6- and 7-positions are observed at 5.92 (2H, *s*) and 4.64 (2H, broad). These results indicate the two methyl groups at the 5- and 8-positions in the same environment, but the two methylene groups are disordered and the proton coupling between these and the geminal coupling are not observed.

To confirm the molecular structure of **3**, optimization of the structure was conducted by the ab initio method using the previously reported method [4]. The calculated structure is shown in Fig. 1. Planar π-conjugation is observed in the diaminomaleonitrile moiety but the other parts, including two azomethine groups, deviated around 20° from the former π-conjugated moiety. The 5,8-dimethyl groups deviated 51° and the ethylene moiety deviated 44° from the azomethine bonds, respectively. From these results, it is proposed that the methyl and methylene groups of **3** have less reactivity for **4** in comparison with the methyl groups of **2**. The reaction of **3** with **4** gave **14** which was reacted at the 6-methylene but not the 5-methyl group. The reason is not clear but the smaller angle of 44° for the ethylene groups have much more possibility to form the enamine in comparison with 51° of the methyl groups. Discrepancy in chemical shift of the methylene groups in the ethylene bridge is not reproduced by the optimized structure but equivalence of the



Scheme 1.

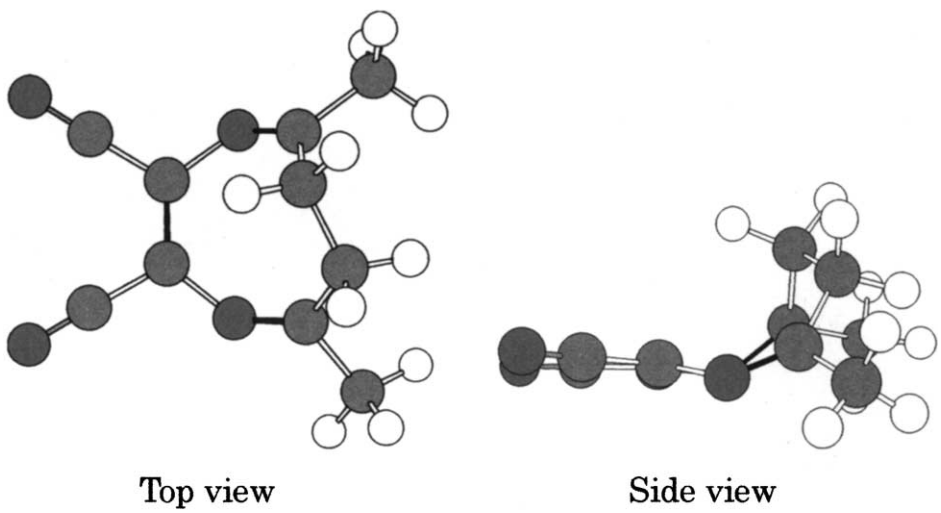


Fig. 1. Optimized molecular structure of **3** calculated by the ab initio method (RHF/3-21G*).

5,8-dimethyl groups is well reproduced. These observations are well in accordance with the NMR results.

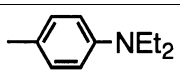
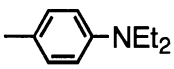
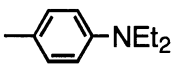
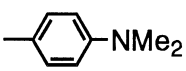
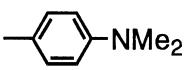
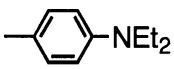
Compound **1** has a planar structure and the two methyl groups at the 5- and 6-positions are observed at 2.72 ppm as a singlet [6]. On the other hand, two methyl groups at the 5- and 7-positions of **2** are observed at a 2.30 ppm as a singlet [3], and those of **3** are 2.13 ppm as a singlet. These chemical shift values indicate an acidity, and hence reactivity of the methyl group in the order **1** > **2** > **3** for the first condensation reaction. As a result, **3** did not give **7** or the corresponding monostyryl dye but gave **14** in poor yield. Compound **1** also did not give **5** because of the full conjugation of the pyrazine ring. Substitution of the styryl group having a strong donor may decrease the reactivity of the second methyl group through π-conjugation.

2.3. Visible and fluorescent spectra of new styryldiazepine dyes

It is already known that styryldicyanodiazepine dyes have a strong intramolecular charge-transfer chromophoric system in their visible spectra and exhibit large Stokes shift in their fluorescence spectra [3]. The visible and fluorescent spectra in chloroform are collated in Table 1 from which the consequences of ring size are apparent.

In a series of monostyryl dyes, exemplified by **8d**, **9d** and **14d**, a hypsochromic shift is observed in both visible and fluorescence spectra as the ring size increases from six to eight. The differences of these values are shown by $\Delta\lambda$ and ΔF values. It is well known that ε_{max} values reflect the molecular planarity and enlargement of π-conjugation. Here, the donor moieties are the same but the acceptor moieties (the ring size and conjugation) are different. As a result, **14d** has the biggest ε_{max} value of 59,500 and **9d** has the smallest of 42,400. It is of interest that the ring size between **9d** and **14d** affects largely on their absorption properties. In a series of bis(styryl) derivatives, two types of derivatives **5c** and **6a**–**6e** could be synthesized. Compound **5c** was known from our previous work and was synthesized by the corresponding Wittig reagent with arylaldehyde [8]. The absorption and fluorescence spectra produce a bathochromic shift from **5c** to **6c**. The Stokes shift (SS) was largest in **9d** and **6c** but that of **14d** was the smallest at 63 nm, and the bis(styryl) dyes have larger SS values

Table 1
Effect of ring size on their spectral properties of diazepine and related fluorescent dyes

Dye No.	Ring size	Aryl substituent	λ_{max}[a]	$\Delta\lambda$	ε_{max}	F_{max}[a]	ΔF	SS[b]
8d	6		513	–	48500	598	–	85
9d	7		493	−20	42400	591	−7	98
14d	8		485	−28	59500	548	−50	63
5c	6		492[c]	–	–	595[c]	–	103
6c	7		523	31	31000	643	48	120
6d	7		539	47	33400	653	58	114

[a] Measured in chloroform at the concentration of 3×10^{-5} mol/l.
[b] Stokes shift, $F_{max} - \lambda_{max}$
[c] Ref. [8]

than the corresponding monostyryl dyes. The ε value of **6d** (33,400) is smaller than that of **9d** (42,400) because of broad absorption curves of **6d**. The ε value corresponds to the area of absorption curve and, in practice, **6d** has a bigger area than that of **9d** (Fig. 2).

Dye **9d** shows a single absorption band, whereas **6d** shows three overlapping peaks in the visible region. The ZINDO MO calculations were conducted by using the optimized structures of **6d** and **9d**. Related energy levels concerned with visible absorption are summarized in Fig. 3.

In the case of monostyryl dye **9d**, the corresponding first excitation is due to the transition from HOMO to LUMO and the calculated ε value is 70,000. On the other hand, dye **6d** has three transitions having the calculated ε values of 80,000, 43,000 and 33,000, respectively. The total calculated ε value of **6d** is 156,000 and is more than twice of that of **9d** (70,000). From these results, dye **6d** has two similar chromophoric systems with an intramolecular charge-transfer character, and the two degenerated HOMOs are split to give one of higher energy and one of lower energy than the corresponding value for **9d**. As a result, the calculated three allowed transitions in **6d** correspond to HOMO–LUMO, $HOMO_1$–LUMO and NHOMO–LUMO (see Fig. 3). These calculated spectral results are well in accordance with the observed results in each case of **6d** and **9d**.

2.4. X-ray crystal structure of *6d*

Bis(styryl) dye **6d** has anomalous broad visible absorption spectra and is proposed to have slightly distorted π-conjugation systems between the two donor–acceptor chromophoric systems. The calculated optimized molecular structure by MOPAC PM3 method showed some distortion between the two chromophores in comparison with the corresponding monostyryl dye **9d** (Fig. 4).

The single crystal of **6d** was successfully obtained from methanol solution by slow evaporation of the solvent. The results of X-ray crystal analysis of **6d** are summarized in Ref. [9]. The molecular structure of **6d** in crystal is shown in Fig. 5.

The 6-methylene group is significantly rotated out of conjugation with the π-electron system of the dicyanodiazepine moiety and it is confirmed that **6d** has a non-planar molecular structure. Two of the 4-(diethylamino)styryl groups as donors do not lie in the same plane and are rotated with respect to each other. These X-ray crystal structures are well reproduced by the MOPAC calculated one (Fig. 4). Molecular stacking of **6d** in crystal is shown in Fig. 6.

The intermolecular interactions between two layers are shown in the top view. Only the phenyl groups overlapped with each other and less molecular overlaps are observed. The interlayer distance of two layers is more than 4 Å which indicates strong intermolecular π–π interactions do not exist as indicated by the side view. These results indicate that non-planar molecular structures of dicyanodiazepine fluorescent dyes prevent strong intermolecular π–π interactions which are necessary to prevent the fluorescence quenching in the solid state. The relationship between solid state fluorescent quenching and molecular structure with respect to intermolecular π–π interactions was studied in detail in pyrazine [10] and bisazomethine chromophores [11].

3. Experimental

3.1. Materials and equipment

The ^{1}H-NMR spectra were taken on a Varian Unity-plus 300 and 500-NMR spectrometers in deuterio-chloroform, deuterio-dimethyl sulfoxide or deuterio-acetone with tetramethylsilane as an internal standard. The mass spectra were recorded on a Shimadzu GCMS-QP5000 spectrometer. The visible and fluorescence spectra were measured on a Hitachi U-2010 spectrophotometer and a Hitachi F-4500 Fluorescence Spectrophotometer, respectively. Melting points were determined on a Yamato melting point apparatus (MP-21) without correction. Elemental analyses were conducted with a Yanaco CHN MT-3 recorder. Wako gel C-300 (silica gel) was used for column chromatography.

Diaminomaleonitrile was supplied by Nippon Soda Co., Ltd. 1-Dimethylaminobutane-1,3-dione and 3-(acetyl)oxacyclopentane-2-one were supplied

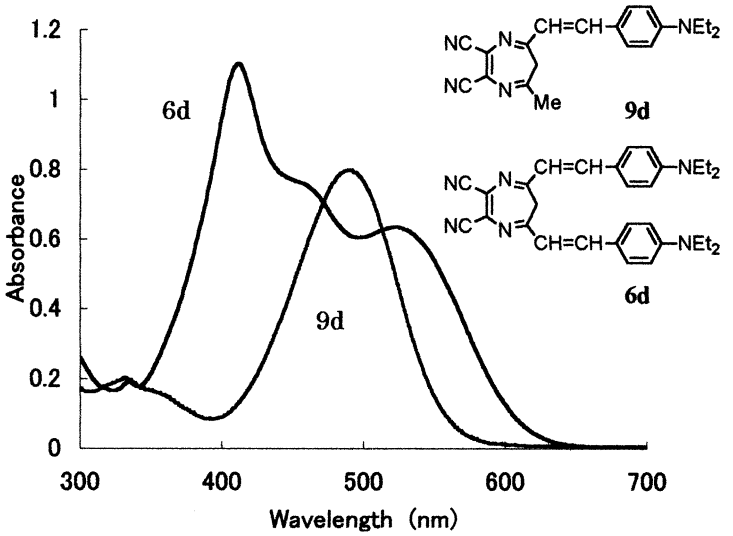


Fig. 2. Comparison of the absorption spectra between **6d** and **9d**.

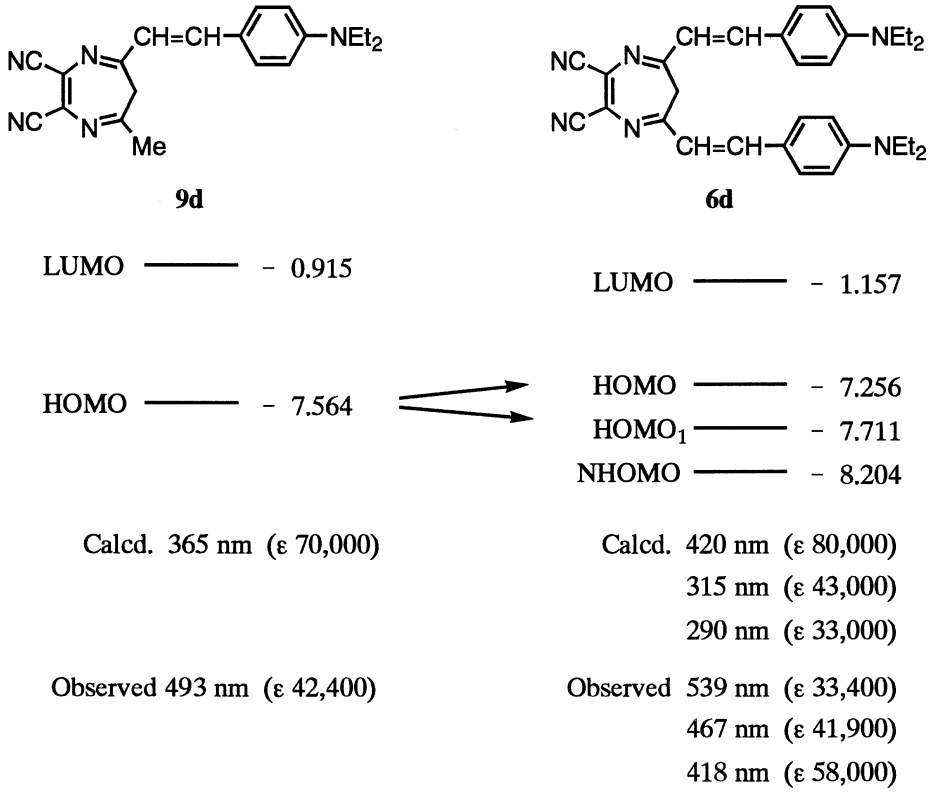


Fig. 3. Comparison of calculated absorption spectra between **6d** and **9d** by ZINDO MO method. Differences in energy levels of related frontier MOs and splitting of HOMO in **6d**.

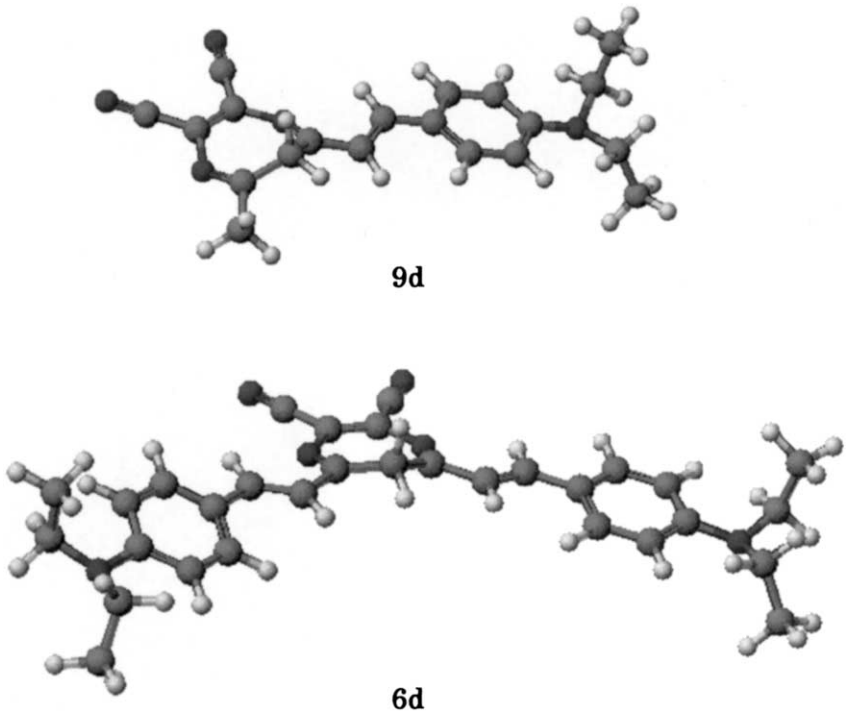


Fig. 4. Optimized structures of **6d** and **9d** calculated by MOPAC PM3 method.

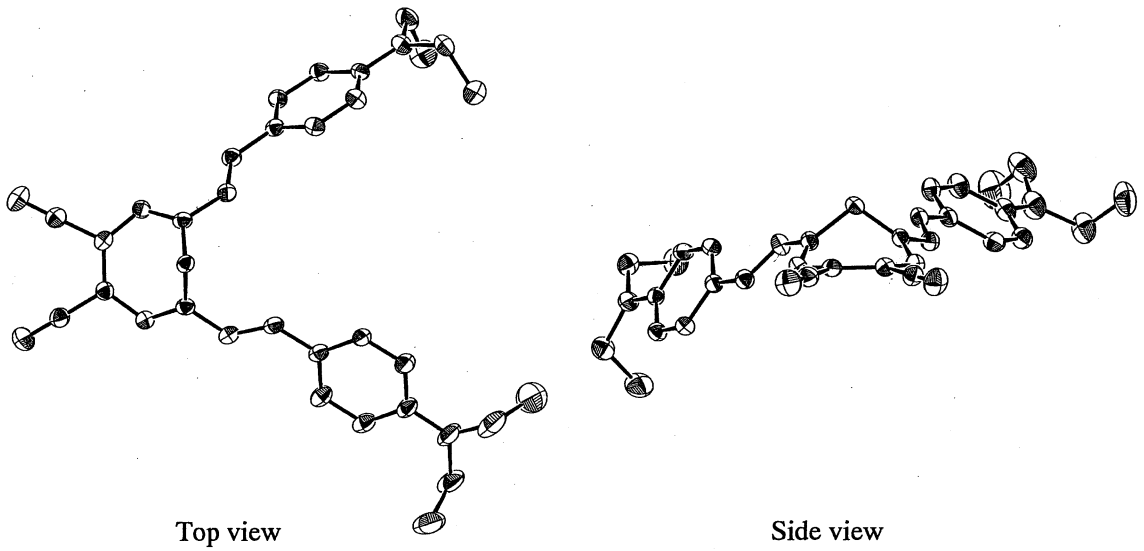


Fig. 5. X-ray crystal structure of **6d**.

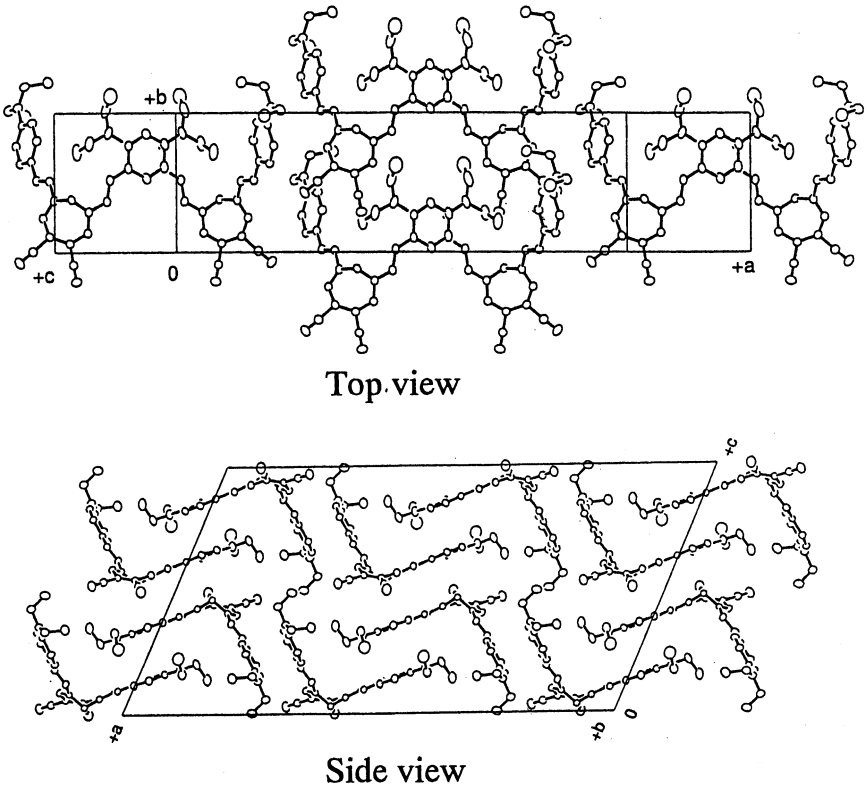


Fig. 6. Molecular stacking of **6d** in single crystal.

by Daicel Chemical Industries, Ltd. Other reagents are commercially available and were used without purification. Compounds **1** [5] and **2** [3] are already known.

3.2. Syntheses of 2,3-dicyano-5,8-dimethyl-1,4-diazacycloocta-2,4,8-triene *3*

A mixture of diaminomaleonitrile (10 mmol), hexane-2,5-dione (10 mmol) and oxalic acid (30 mg) in benzene (50 ml) was refluxed for 3 h in a flask equipped with a Dean–Stark trap to remove generated water. The mixture was cooled at room temperature and benzene was removed in vacuo. The residue was washed with water and filtered. The precipitate was recrystalized from methanol to give **3**.

Yield: 55%, mp: 158–159 °C; δ_H ($CDCl_3$) 5.92 (2H, *s*, CH_2), 4.64 (2H, broad, CH_2), 2.13 (6H, *s*, $2CH_3$); mass (*m*/*e*): 186 (M^+); Anal. calcd. for $C_{10}H_{10}N_4$: (C, 64.50; H, 5.41; N, 30.09%), found: (C, 64.83; H, 5.48; N, 30.13%).

3.3. Syntheses of 2,3-dicyano-5,7-bis(styryl)-6H-1,4-diazepine *6* and 2,3-dicyano-5-methyl-6-styrylpyrazine *8* (general procedure)

A mixture of 2,3-dicyano-5,6-dimethylpyrazine **1** (10 mmol) or 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine **2**, arylaldehyde **4** (10 mmol) and several drops of piperidine in benzene (50 ml) was refluxed for 6 h in a flask equipped with a Dean–Stark trap to remove generated water. The mixture was cooled at room temperature and benzene was evaporated. The precipitate was collected, dried and purified by column chromatography on silica gel using chloroform as an eluent and then by recrystalization to give **8** or **6**.

2,3-Dicyano-5,7-bis[2-(4-methoxyphenyl)ethenyl]-6*H*-1,4-diazepine **6a**: yield: 10%, mp: 259–260 °C;

δ_H ($CDCl_3$) 7.54 (2H, *dd*, $J=15.9$, 3.0 Hz, 2CH), 7.49 (4H, *d*, $J=8.7$, Ph), 6.76 (2H, *dd*, $J=15.9$, 3.0, 2CH), 6.93 (4H, *d*, $J=8.7$, 2.4, Ph), 3.85 (6H, *s*, $2OCH_3$) ; δ_H (d_6-DMSO) 8.05 (2H, *d*, $J=16.5$, 2CH), 7.75 (4H, *d*, $J=7.2$, Ph), 7.00 (4H, *d*, $J=7.2$, Ph), 7.00 (2H, *d*, $J=16.5$, 2CH), 5.35 (1H, broad, CH), 3.81 (6H, *s*, $2OCH_3$), 2.05 (1H, broad, CH). The CH_2 signal at the 6-methylene was not observed because of broadening of the signals but that in d_6-DMSO was observed at 5.35 and 2.05 ppm, respectively; mass (*m*/*e*): 408 (M^+); UV: λ_{max} 434 nm (ε 24,200), F_{max} 542 nm; anal. calcd. for $C_{25}H_{20}N_4O_2$: (C, 73.51; H, 4.94; N, 13.72%), found: (C, 74.00; H, 5.12; N, 13.58%).

2,3 - Dicyano - 5,7 - bis[2 - [4 - (dimethylamino)-phenyl]ethenyl]-6*H*-1,4-diazepine **6c**: yield: 74%, mp: 260–262 °C; mass (*m*/*e*): 434 (M^+) ; UV: λ_{max} 523 nm (ε 31,000), F_{max} 643 nm; anal. calcd. for $C_{27}H_{26}N_6$: (C, 74.63; H, 6.03; N, 19.34%), found: (C, 73.92; H, 6.07; N, 18.93%).

2,3-Dicyano-5,7-bis[2-[4-(diethylamino)phenyl] ethenyl]-6*H*-1,4-diazepine **6d**: yield: 14%, mp: 209–211 °C; δ_H (d_6-DMSO) 7.93 (2H, *d*, $J=16.0$, 2CH), 7.81 (4H, *d*, $J=9.0$, Ph), 6.79 (2H, *d*, $J=16.0$, 2CH), 6.68 (4H, *d*, $J=9.0$, Ph), 3.40 (8H, *q*, $J=7.0$, $4CH_2$), 2.09 (2H, *s*, CH_2), 1.09 (12H, *t*, $J=7.0$, $4CH_3$); δ_H (d_6-acetone) 7.906 (2H, *d*, $J=16.0$, 2CH), 7.602 (4H, *d*, $J=8.0$, Ph), 6.763 (2H, *d*, $J=$ 16.0, 2CH), 6.736 (4H, *d*, $J=8.0$, Ph), 3.470 (8H, *q*, $J=7.0$, $4CH_2$), 2.813 (2H, *s*, CH_2), 1.167 (12H, *t*, $J=7.0$, $4CH_3$); mass (*m*/*e*): 490 (M+); UV: λ_{max} 539 nm (ε 33,400), F_{max} 653 nm; anal. calcd. for $C_{31}H_{34}N_6$: (C, 75.89; H, 6.98; N, 17.13%), found: (C, 76.34; H, 7.30; N, 17.12%).

2,3-Dicyano-5,7-bis[2-(julolidin-9-yl)ethenyl]-6*H*-1,4-diazepine **6e**: yield: 50%, mp: >300 °C; mass (*m*/*e*): 538 (M^+); UV: λ_{max} 569 nm (ε 30,600), F_{max} 682 nm; anal. calcd. for $C_{35}H_{34}N_6$: (C, 78.04; H, 6.36; N, 15.60%), found: (C, 77.36; H, 6.47; N, 14.99%).

2,3-Dicyano-5-methyl-6-[2-[4-(diethylamino)-phenyl]ethenyl]pyrazine **8d**: yield: 8%, mp: 211–212 °C; mass (*m*/*e*): 317 (M^+); UV: λ_{max} 513 nm (ε 48,500), F_{max} 598 nm; anal. calcd. for $C_{19}H_{19}N_5$: (C, 71.90; H, 6.03; N, 22.07%), found: (C, 71.87; H, 6.15; N, 21.51%).

Synthesis of **7** was unsuccessful by this method and only the corresponding mono-substituted derivatives **14**, 2,3-dicyano-5,8-dimethyl-6-styryl cyclooctane-2,4,8-trienes, were obtained.

Compounds **8c** [6] and **9**–**13** were synthesized by the method previously reported [3], and are identified in the following. Dye **5c** [8], and dyes **9d**, **10a**, **10c**–**10e**, **11d**, **12d** and **13d** were previously reported [3].

2,3-Dicyano-5-methyl-7-[2-[4-(dimethylamino)-phenyl]ethenyl]-6*H*-1,4-diazepine **9c**: yield: 18%, mp: >300 °C; δ_H ($CDCl_3$) 7.47 (2H, *d*, $J=9.0$, Ph), 7.46 (1H, *d*, $J=15.9$, CH), 6.69 (1H, *d*, $J=15.9$, CH), 6.69 (2H, *d*, $J=9.0$, Ph), 4.60 (1H, broad, CH), 3.08 (3H, *s*, NCH_3), 3.07 (3H, *s*, NCH_3), 2.22 (3H, *s*, CH_3), 1.80 (1H, broad, CH); mass (*m*/*e*): 303 (M^+); UV: λ_{max} 475 nm (ε 31,000), F_{max} 587 nm; anal. calcd. for $C_{18}H_{17}N_5$: (C, 71.26; H, 5.65; N, 23.09%), found: (C, 71.23; H, 5.94; N, 22.58%).

2,3-Dicyano-5-phenyl-7-[2-(*N*-ethylcarbazol-3-yl) ethenyl]-6*H*-1,4-diazepine **10b**: yield: 66%, mp: 256–259 °C; δ_H (d_6-DMSO) 8.57 (1H, *s*, Ph), 8.27 (2H, *d*, $J=7.5$, Ph), 8.18 (1H, *d*, $J=7.8$, Ph), 8.18 (1H, *d*, $J=16.2$, CH), 7.82 (1H, *d*, $J=8.7$, Ph), 7.66 (1H, *d*, $J=9.0$, Ph), 7.66 (1H, *d*, $J=9.0$, Ph), 7.58 (3H, *m*, Ph), 7.51 (1H, *t*, $J=7.8$, Ph), 7.28 (1H, *t*, $J=7.5$, Ph), 7.15 (1H, *d*, $J=16.2$, CH), 5.85 (1H, broad, CH), 4.46 (2H, *q*, $J=6.9$, CH_2), 2.27 (1H, broad, CH), 1.31 (3H, *t*, $J=6.9$, CH_3) ; mass (*m*/*e*): 439 (M^+); UV: λ_{max} 461 nm (ε 29,700), F_{max} 571 nm; anal. calcd. for $C_{29}H_{21}N_5$: (C, 79.25; H, 4.82; N, 15.94%), found: (C, 79.00; H, 5.06; N, 15.75%).

2,3-Dicyano-5-ethoxy-5-hydroxy-6-[4-(methoxy) phenyl]methylidene]-7-methyl-4*H*-1,4-diazepine **11a**: yield: 61%, mp: 162–163 °C; mass (*m*/*e*): 338 (M^+); UV: λ_{max} 427 nm (ε 28,100), F_{max} 493 nm; anal. calcd. for $C_{18}H_{18}N_4O_3$: (C, 63.89; H, 5.36; N, 16.56%), found: (C, 62.98; H, 5.39; N, 15.60%).

2,3-Dicyano-5-ethoxy-5-hydroxy-6-[(*N*-ethylcarbazol-3-yl)methylidene]-7-methyl-4*H*-1,4-diazepine **11b**: yield: 57%, mp: 210–211 °C; mass (*m*/*e*): 425 (M^+); UV: λ_{max} 457 nm (ε 32,200), F_{max} 518 nm; anal. calcd. for $C_{25}H_{23}N_5O_2$: (C, 70.57; H, 5.45; N, 16.46%), found: (C, 70.66; H, 5.62; N, 16.14%).

2,3-Dicyano-5-ethoxy-5-hydroxy-6-[(julolidin-9-yl) methylidene]-7-methyl-4*H*-1,4-diazepine **11e**: yield:

43%, mp: 202–205 °C; δ_H ($CDCl_3$) 12.07 (1H, *s*, NH), 8.20 (1H, *s*, OH), 7.57 (2H, broad, Ph), 4.94 (1H, *s*, CH), 4.25 (2H, *q*, $J=7.2$, OCH_2), 3.32 (4H, *t*, $J=6.0$, $2CH_2$), 2.78 (4H, *t*, $J=6.0$, $2CH_2$), 2.37 (3H, *s*, CH_3), 1.97 (4H, *q*, $J=6.0$, $2CH_2$), 1.32 (3H, *t*, $J=7.2$, CH_3); mass (*m*/*e*): 403 (M^+); UV: λ_{max} 523 nm (ε 45,600), F_{max} 573 nm; anal. calcd. for $C_{23}H_{25}N_5O_2$: (C, 68.47; H, 6.25; N, 17.36%), found: (C, 68.90; H, 6.38; N, 17.04%).

2,3-Dicyano-5-dimethylamino-5-hydroxy-6-[4-(methoxy)phenyl]methylidene]-7-methyl-4*H*-1,4-diazepine **12a**: yield: 3%, mp: 171–172 °C; mass (*m*/*e*): 337 (M^+); UV: λ_{max} 435 nm (ε 29,500), F_{max} 501 nm; anal. calcd. for $C_{18}H_{19}N_5O_2$: (C, 64.08; H, 5.68; N, 20.76%), found: (C, 64.72; H, 5.69; N, 19.96%).

2,3-Dicyano-5-dimethylamino-5-hydroxy-6-[(*N*-ethylcarbazol-3-yl)methylidene]-7-methyl-4*H*-1,4-diazepine **12b**: yield: 15%, mp: 188–189 °C; mass (*m*/*e*): 424 (M^+); UV: λ_{max} 458 nm (ε 31,900), F_{max} 519 nm; anal. calcd. for $C_{25}H_{24}N_6O$: (C, 70.73; H, 5.70; N, 19.80%), found: (C, 70.68; H, 5.82; N, 19.80%).

2,3-Dicyano-5-dimethylamino-5-hydroxy-6-[(julolidin-9-yl)methylidene]-7-methyl-4*H*-1,4-diazepine **12e**: yield: 60%, mp: 177–178 °C; mass (*m*/*e*): 402 (M^+); UV: λ_{max} 523 nm (ε 41,000), F_{max} 569 nm; anal. calcd. for $C_{23}H_{26}N_6O$: (C, 68.63; H, 6.51; N, 20.88%), found: (C, 68.82; H, 6.74; N, 20.19%).

2,3-Dicyano-4*a*-hydroxy-8-(4-methoxyphenyl)-9-methyl-4*H*,6*H*,7*H*-oxacyclohexano[2,3-*e*]-1,4-diazepine **13a**: yield: 21%, mp: 203–206 °C; mass (*m*/*e*): 336 (M^+); UV: λ_{max} 437 nm (ε 28,400), F_{max} 510 nm; anal. calcd. for $C_{18}H_{16}N_4O_3$: (C, 64.28; H,4.80; N, 16.66%), found: (C, 64.07; H, 4.85; N, 16.27%).

2,3-Dicyano-4*a*-hydroxy-8-(*N*-ethylcarbazol-3-yl)-9-methyl-4*H*,6*H*,7*H*-oxacyclohexano[2,3-*e*]-1,4-diazepine **13b**: yield: 64%, mp: 217–220 °C; mass (*m*/*e*): 423 (M^+); UV: λ_{max} 463 nm (ε 33,600), F_{max} 528 nm; anal. calcd. for $C_{25}H_{21}N_5O_2$: (C, 70.91; H, 5.00; N, 16.54%), found: (C, 70.34; H, 5.05; N, 16.37%).

2,3-Dicyano-4*a*-hydroxy-8-[4-(dimethylamino)-phenyl]-9-methyl-4*H*,6*H*,7*H*-oxacyclohexano[2,3-*e*]-1,4-diazepine **13c**: yield: 71%, mp: 219–221 °C; δ_H (d_6-DMSO) 11.55 (1H, *s*, NH), 8.30 (1H, *s*, OH), 7.95 (2H, *d*, $J=7.2$, Ph), 6.97 (2H, *d*, $J=7.2$, Ph), 4.37 (2H, *t*, $J=7.5$, CH_2), 3.07 (3H, *s*, CH_3), 2.96 (2H, *t*, $J=7.5$, CH_2), 2.50 (6H, *s*, NMe_2); mass (*m*/*e*): 349 (M^+); UV: λ_{max} 501 nm (ε 37,600), F_{max} 550 nm; anal. calcd. for $C_{19}H_{19}N_5O_2$: (C, 65.31; H, 5.48; N, 20.05%), found: (C, 65.77; H, 5.68; N, 19.94%).

2,3-Dicyano-4*a*-hydroxy-8-(julolidin-9-yl)-9-methyl-4*H*,6*H*,7*H*-oxacyclohexano[2,3-*e*]-1,4-diazepine **13e**: yield: 50%, mp: 214–216 °C; mass (*m*/*e*): 401 (M^+); UV: λ_{max} 532 nm (ε 48,000), F_{max} 585 nm; anal. calcd. for $C_{23}H_{23}N_5O_2$: (C, 68.81; H, 5.77; N, 17.45%), found: (C, 68.65; H, 5.89; N, 17.07%).

2,3-Dicyano-5,8-dimethyl-6-[2-[4-(dimethylamino)phenyl]ethenyl]-1,4-diazacyclooctane-2,4,8-triene **14c**: yield: 10%, mp: 169–171 °C; δ_H ($CDCl_3$) 8.593 (1H, *s*, CH), 7.896 (2H, broad, Ph), 6.740 (2H, *d*, $J=9.0$, Ph), 5.936 (2H, *s*, CH_2), 3.161 (6H, *s*, NMe_2), 2.256 (6H, *s*, $2CH_3$); mass (*m*/*e*): 317 (M^+); UV: λ_{max} 474 nm (ε 54,300), F_{max} 546 nm. 2,3-Dicyano-5,8-dimethyl-6-[2-[4-(diethylamino)-phenyl]ethenyl]-1,4-diazacyclooctane-2,4,8-triene **14d**: yield: 6%, mp: 142–144 °C; δ_H (d_6-acetone) 8.557 (1H, *s*, CH), 7.873 (2H, broad, Ph), 6.719 (2H, *d*, $J=9.0$, Ph), 5.933 (2H, *s*, CH_2), 3.495 (4H, *q*, $J=7.0$, $2CH_2$), 2.255 (6H, *s*, $2CH_3$), 1.260 (6H, *t*, $2CH_3$); mass (*m*/*e*): 345 (M^+); UV: λ_{max} 485 nm (ε 59,500), F_{max} 548 nm; anal. calcd. for $C_{21}H_{23}N_5$: (C, 73.01; H, 6.71; N, 20.27%), found: (C, 73.21; H, 7.15; N, 19.46%).

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