

Synthesis of Near-Infrared Fluorescent 2,3-Dicyano-6*H*-1,4-diazepines

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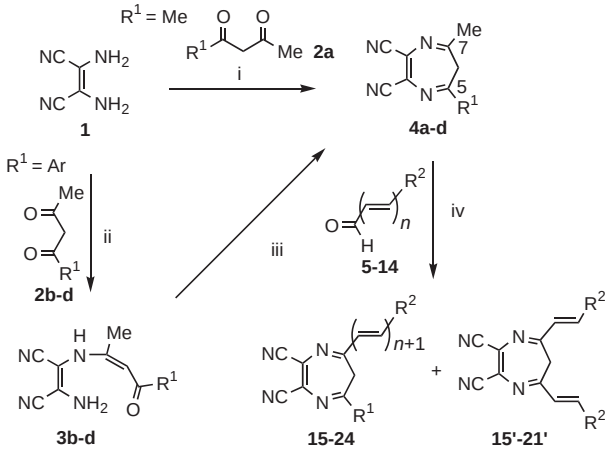
A series of novel 5-(2-arylethenyl)-, 5-(4-arylbutadienyl)-, 5-(6-arylhexatrienyl)-, and 5-(8-octatetraenyl)-, 5-aryl-7-(2-arylethenyl)-, and 5,7-bis(2-arylethenyl)-2,3-dicyano-6*H*-1,4-diazepines were synthesized by the reactions of 2,3-dicyano-5-methyl-6*H*-1,4-diazepines with aromatic aldehydes. These compounds showed intramolecular charge-transfer chromophoric systems from the arylethenyl to the 2,3-dicyano-6*H*-diazepine moieties. The shifts in UV–vis absorption bands were estimated by calculating the HOMO and LUMO energy levels. 2-(9-Julolidyl)ethenyl derivative showed the most intense fluorescence. The 6-(9-julolidyl)-1,3,5-hexatrienyl and 8-(9-julolidyl)-1,3,5,7-octatetraenyl derivatives exhibited the fluorescence maxima (F_{max}) at 780 and 842 nm, respectively.

Near-infrared fluorescent dyes have potential applications as fluorescent labeling reagents, laser dyes, and biological probes.[1] Though several bathochromic fluorescence dyes such as polymethines,[2] cyanines,[3] rhodamines,[4] squaryliums,[5] styryls,[6] naphthalocyanines,[7] and ytterbium(III) complexes[8] have been reported, they have either ionic structure or metal–complex structure. To our knowledge, few bathochromic fluorescent dyes having a neutral structure are known. Only quaterrylene bisimides[9] and pyrans[10] have been reported. Therefore, it is of significance to obtain neutral near-infrared fluorescent compounds. In our series of studies on 2,3-dicyano-6*H*-1,4-diazepines, it was found that they showed F_{max} around 600 nm and that the introduction of a bulky substituent at the 6-position enhanced fluorescence intensity in solid state.[11] We report herein the synthesis of near-infrared fluorescent 2,3-dicyano-6*H*-1,4-diazepine derivatives.

Results and Discussion

2,3-Dicyano-6*H*-1,4-diazepines **15**–**24** and **15′**–**21′** were prepared as shown in Scheme 1. Diaminomaleonitrile (DAMN, **1**) reacted with acetylacetone (**2a**) in the presence of oxalic acid to give 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (**4a**) in a 78% yield. Compound **1** also reacted with aroylacetones **2b–d** to afford the open-ring intermediates **3b–d**, which were cyclized in the presence of diphosphorus pentaoxide to provide 5-aryl-2,3-dicyano-7-methyl-6*H*-1,4-diazepines **4b–d** in 27–67% yields. Then, the condensation of **4a–d** with aldehydes **5**–**14** gave the 5-(2-arylethenyl)-, 5-(4-aryl-1,3-butadienyl)-, 5-(6-aryl-1,3,5-hexatrienyl)-, and 5-(8-aryl-1,3,5,7-octatetraenyl)-, 5-aryl-7-(2-arylethenyl), and 5,7-bis(2-arylethenyl)-2,3-dicyano-6*H*-1,4-diazepines **15**–**24** and **15′**–**21′**.

The reactions of **4a–d** with aromatic aldehydes **5**–**14** are given in Table 1. When **4a** reacted with a molar amount of unsubstituted and electron-deficient aromatic aldehydes **5** and **6** and heteroaromatic aldehydes **9**, **10**, and **11**, 5,7-bis(arylethenyl) derivatives **15′**, **16′**, **19′**, **20′**, and **21′** were obtained as main products together with 5-(arylethenyl) derivatives **15**, **16**, **19**, **20**, and **21** (runs 1, 2, and 9–11). The yields of products in the reaction of **4a** with **5** and **6** were rather low, due to formation of unidentified products which were not developed by column chromatography. Meanwhile, when **4a** reacted with a molar amount of electron-donating aromatic aldehydes such as **7** and **8**, 5-(2-arylethetnyl) derivatives **17** and **18a** were obtained as main products together with a trace amount of 5,7-bis(2-arylethenyl) derivatives **17′** and **18′a**, respectively (runs 3 and 4). These results suggest that the acidity of methyl-protons at both the 5- and 7-positions in **4a** is high enough to easily react with aromatic aldehydes and that the product distribution depends on the electronic effect of the aldehydes. Compound **4a** reacted with two molar amounts of **8** to give the 5,7-bis(2-arylethenyl)



2a, 4a: R^1 = Me, **2b, 4b**: R^1 = Ph

2c, 4c: R^1 = $C_6H_4NMe_2$ (*p*), **2d, 4d**: R^1 = C_6H_4CN (*p*)

n = 0, 1, 2, 3 R^2 = shown in Table 1

Scheme 1. Reagents and conditions: i) acetylacetone (1.0 mol. amt.), oxalic acid (trace), benzene, reflux, ii) aroylacetones (1.0 mol. amt.), oxalic acid (trace), benzene, reflux, iii) diphosphorus pentaoxide, ethanol, reflux, iv) 2,3-dicyano-7-methyl-6*H*-1,4-diazepines (1.0 mol. amt.), aldehydes (1.0–2.0 mol. amt.), piperidine (a few drops), benzene, 50 °C–reflux.

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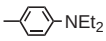
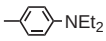
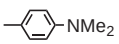
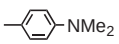
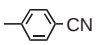
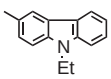
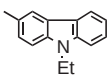
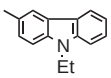
Table 1. Synthesis of 2,3-Dicyano-6*H*-1,4-diazepines

Run	Starting materials					Products				
	Dicyanodiazepines		Aldehydes							
	Compd	R^1	Compd	R^2	*n*	Compd	R^1	R^2	*n*	Yield[a]/%
1	**4a**	Me	**5**		0	**15**	Me		0	9
						15′	—		0	10
2	**4a**	Me	**6**		0	**16**	Me		0	11
						16′	—		0	20
3	**4a**	Me	**7**		0	**17**	Me		0	50[b]
4	**4a**	Me	**8**		0	**18a**	Me		0	20[b]
5[c]	**4a**	Me	**8**		0	**18′a**	—		0	50
6	**4b**		**8**		0	**18b**			0	28
7	**4c**		**8**		0	**18c**			0	56
8	**4d**		**8**		0	**18d**			0	38
9	**4a**	Me	**9**		0	**19**	Me		0	6
						19′	—		0	50
10	**4a**	Me	**10**		0	**20**	Me		0	7
						20′	—		0	90
11	**4a**	Me	**11**		0	**21**	Me		0	6
						21′	—		0	80
12	**4a**	Me	**12**		1	**22**	Me		1	10
13	**4a**	Me	**13**		2	**23**	Me		2	18
14	**4a**	Me	**14**		3	**24**	Me		3	16

a) Isolated yields. b) A trace amount of 5,7-bis(2-arylethenyl) derivative was also produced. c) Two molar amounts of **8** were used.

derivative **18′a** in a 50% yield (run 5). 5-Aryl-2,3-dicyano-7-methyl-6*H*-1,4-diazepines **4b–d** reacted with **8** to afford the corresponding 5-aryl-7-(2-arylethenyl) derivatives **18b–d** in moderate yields (runs 6–8). Compound **4a** also reacted with olefinic aldehydes **12–14** to provide the 5-[4-(9-julolidyl)-1,3-butadienyl)], 5-[6-(9-julolidyl)-1,3,5-hexatrienyl], and 5-[8-(9-julolidyl)-1,3,5,7-octatetraenyl] derivatives **22–24** in low yields along with formation of unidentified products which were not developed by column chromatography (runs 12–14).

The UV–vis absorption and fluorescence spectra of **18a**, **18c**, and **18′a** are shown in Fig. 1. The λ_{max} of **18a** was observed at 519 nm with a molar absorption coefficient (ε) of 34800 $dm^3\,mol^{-1}\,cm^{-1}$. The F_{max} was observed at 640 nm, the Stokes shift being 121 nm (3643 cm^{-1}). The fluorescence quantum yield was calculated to be 0.19. Compound **18c** showed two absorption bands in the visible region, the λ_{max} being 399 and 530 nm. The F_{max} was observed at 673 nm. Compounds **18′a** showed the λ_{max} at 434, 494, and 568 nm. The F_{max} was observed at 726 nm. Interestingly, the fluorescence of 5-(2-arylethenyl) derivative **18a** was most intense among the 5-(2-arylethenyl), 5-aryl-7-(2-arylethenyl), and 5,7-bis(2-arylethenyl) derivatives **18a**, **18c**, and **18′a**.

The UV–vis absorption and fluorescence spectra of **18a**, **22**, **23**, and **24** are depicted in Fig. 2. As expected, the λ_{max} caused a bathochromic shift from 519 to 580 nm with the expansion of olefinic unit. The bathochromic displacement by ca. 10–30 nm was observed for the expansion of one ethylene unit. The F_{max} also showed a bathochromic shift from 640 to 842 nm. A shift

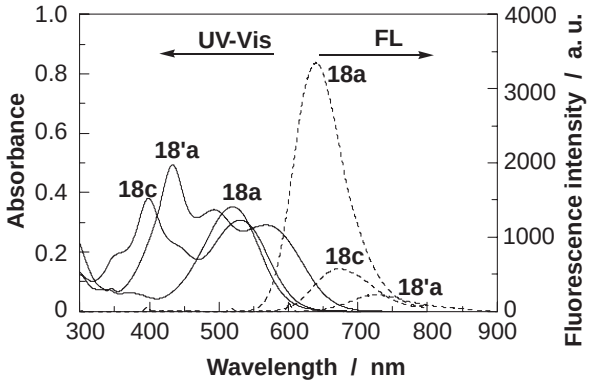


Fig. 1. UV–vis absorption and fluorescence spectra of **18a**, **18c**, and **18′a**. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively. Measured on 1×10^{-5} mol dm^{-3} of substrate at 25 °C.

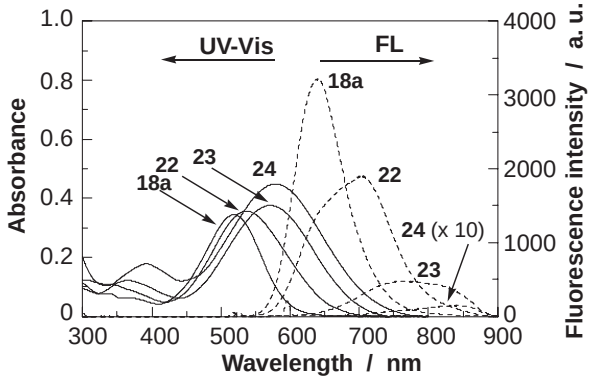


Fig. 2. UV–vis absorption spectra of **18a**, **22**, **23**, and **24**. Solid and dotted lines represent UV–vis absorption and fluorescence spectra, respectively. Measured on 1×10^{-5} mol dm^{-3} of substrate at 25 °C.

Table 2. Observed and Calculated UV–Vis Absorption and Fluorescence Spectra of 2,3-Dicyano-6*H*-1,4-diazepines

Run	Compd	Obsd[a]			RFI	Calcd	
		λ_{max} (ε_{max}) nm	F_{max} nm	Stokes shift nm (cm^{-1})		λ_{max}/nm(f[b])	CI component
1	**15**	360 (28600)	437	77 (4895)	<1	331 (0.64)	HOMO to LUMO (83%)
2	**16**	364 (35200)	437	73 (4590)	<1	331 (0.68)	HOMO to LUMO (84%)
3	**17**	491 (40400)	601	110 (3728)	26	349 (1.01)	HOMO to LUMO (75%)
4	**18a**	519 (34800)	640	121 (3643)	100	352 (1.03)	HOMO to LUMO (72%)
5	**18b**	540 (34800)	684	144 (3899)	58	360 (0.87)	HOMO to LUMO (71%)
		412 (11300)				308 (0.50)	HOMO to LUMO+1 (45%)
							HOMO−1 to LUMO (22%)
6	**18c**	530 (31500)	673	143 (4009)	16	361 (0.78)	HOMO to LUMO (72%)
		399 (39000)				310 (0.79)	HOMO to LUMO+1 (48%)
							HOMO−1 to LUMO (18%)
7	**18d**	571 (40200)	725	154 (3720)	2	377 (1.19)	HOMO to LUMO (74%)
		445 (19500)				317 (0.38)	HOMO to LUMO+1 (35%)
							HOMO−1 to LUMO (18%)
8	**18′a**	568 (28800)	726	158 (3832)	7	368 (0.66)	HOMO to LUMO (69%)
		494 (34000)				321 (1.49)	HOMO to LUMO+1 (54%)
		434 (48900)				306 (0.21)	HOMO−1 to LUMO (43%)
							HOMO−2 to LUMO+1 (23%)
9	**19**	392 (30800)	436	44 (2574)	<1	349 (0.85)	HOMO to LUMO (87%)
10	**20**	392 (36300)	438	46 (2679)	<1	357 (0.91)	HOMO to LUMO (89%)
11	**21**	443 (28800)	556	113 (4587)	2	344 (1.05)	HOMO to LUMO (71%)
12	**22**	536 (35900)	705	169 (4473)	57	385 (1.64)	HOMO to LUMO (80%)
13	**23**	568 (38300)	780	212 (4785)	14	397 (2.02)	HOMO to LUMO (77%)
14	**24**	580 (44900)	842	262 (5365)	1	407 (2.40)	HOMO to LUMO (74%)

a) Measured in chloroform at the concentration of 1×10^{-5} mol dm^{-3}. b) Oscillator strength.

of F_{max} ca. 40–80 nm was observed for the expansion of one ethylene unit. The Stokes shift of **24** was very large: 262 nm (5365 cm^{-1}). The fluorescence intensity decreased by introducing a flexible olefinic moiety, in the order: **18a** > **22** > **23** > **24**. Thus, compounds **23** and **24** showed the F_{max} in the near-infrared region.

The UV–vis absorption and fluorescence spectra of the other derivatives are indicated in Table 2. The λ_{max} of 5-(2-arylethenyl) derivatives having an electron-donating dialkylamino group **17** and **18a** were observed at 491 and 519 nm, respectively; they are much more bathochromic than the unsubstituted and electron-withdrawing ones **15** (360 nm) and **16** (364) (runs 1–4). Heteroaromatic ethenyl derivatives **19** (392), **20** (392), and **21** (443) were more bathochromic than the styryl derivative **15** (360) (runs 1 and 9–11).

5-Aryl-7-(2-arylethenyl) derivatives were slightly more bathochromic in the following order: **18d** (571) > **18b** (540), **18c** (530), **18a** (519) (runs 4–7). Thus, the introduction of an electron-withdrawing group into the phenyl ring at the 5-position caused a slight bathochromic shift. 5,7-Bis(2-arylethenyl) derivative **18′a** (568) was more bathochromic than the 5-(2-arylethenyl) derivative **18a** (519) (runs 4 and 8).

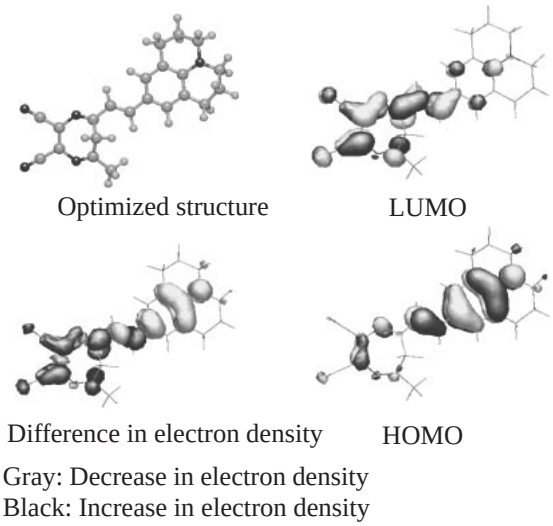


Fig. 3. Schematic representation of optimized structure, HOMO, LUMO, and difference in electron-density between ground and first excited state in **18a**.

5-(2-Arylethenyl) derivative **18a** showed more intense fluorescence than the 5-aryl-7-(2-arylethenyl) and 5,7-bis(2-arylethenyl) derivatives **18b–d** and **18′a** (runs 4–8). The fluorescence intensity of 5-[2-(9-julolidyl)ethenyl] derivative **18a** was highest among the 5-(2-arylethenyl) and 5-(2-heteroarylethenyl) derivatives **15–21** (runs 1–4 and 9–11).

To explain the absorption spectra of 2,3-dicyano-6*H*-1,4-diazepines, we carried out semi-empirical MO calculations using the WinMOPAC 3.0 package (Fujitsu, Chiba, Japan).[12] Geometry optimizations were performed using the AM1 method. Then the absorption spectra were calculated with the INDO/S method. In the calculation, the parameters of the sulfur atom ($Es = 21.02$, $Ep = 10.97$, $Bsp = 13.5$, $G = 10.01$) were added.[13] One hundred configurations were considered for the configuration interaction.

The schematic representation of optimized geometry, HOMO, LUMO, and the difference in electron density between the ground and first excited states in **18a** are shown in Fig. 3. Electrons are located around the julolidyl moiety in the HOMO energy level due to its electron-donating nature. Meanwhile electrons are located around the diazepine ring in the LUMO energy level because of its electron-deficient property. The difference in electron density clearly indicates that the 5-(2-arylethenyl)-2,3-dicyano-6*H*-1,4-diazepines have an intramolecular charge-transfer chromophoric system from the 2-arylethenyl to 2,3-dicyano-6*H*-diazepine moieties.

The results of calculated UV–vis absorption bands are also indicated in Table 2. 5-(2-Arylethenyl), 5-(4-aryl-1,3-butadienyl), 5-(6-aryl-1,3,5-hexatrienyl), and 5-(8-aryl-1,3,5,7-octatetraenyl) derivatives **15–24** showed the first absorption band in the visible region. These absorption bands were attributed to the HOMO to LUMO transition (runs 1–4 and 9–14). Meanwhile, the first and second absorption bands in the 5-aryl-7-(2-arylethenyl) derivatives **18b**, **18c**, and **18d** were characterized as the HOMO to LUMO and a mixture of HOMO to next LUMO (LUMO+1) and next HOMO (HOMO−1) to LUMO transition, respectively (runs 5–7).

The calculated energy levels for 5-(2-arylethenyl) derivatives **15–21** are shown in Fig. 4. The bathochromic shift in **17** and **18a**, compared with **15** and **16**, can be ascribed to large destabilization of HOMO energy level due to the introduction of an electron-donating dialkylamino group into the chromophore. The bathochromic shifts in the 5-[2-(heteroaryl)ethenyl]-7-methyl derivatives **19**, **20**, and **21**, compared with that in the styryl derivative **15**, were also attributed to destabilization of the HOMO energy level because of the electron-sufficient heteroaromatic moiety.

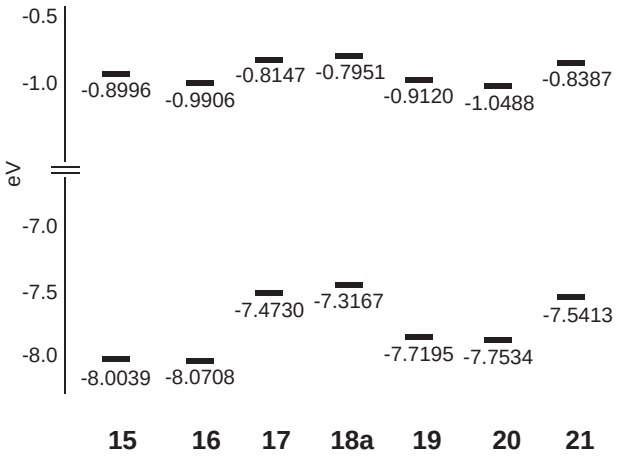


Fig. 4. Energy levels of **15–21**.

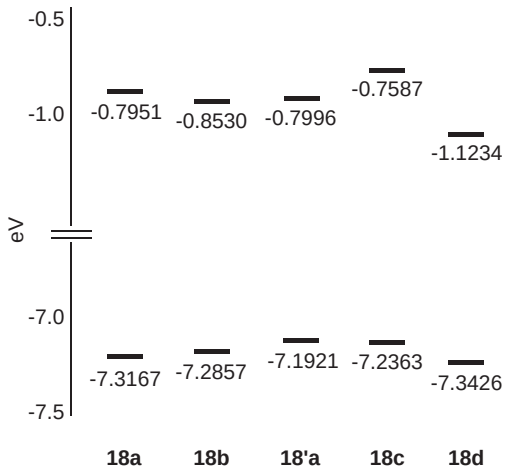


Fig. 5. Energy levels of **18a**, **18b**, **18c**, **18d**, and **18′a**.

The calculated energy levels of 5-(2-arylethenyl), 5-aryl-7-(2-arylethenyl), and 5,7-bis(2-arylethenyl) derivatives **18a–18d** and **18′a** are shown in Fig. 5. The bathochromic shift in the UV–vis absorption band of **18b** and **18′a**, compared to that of **18a**, can be explained by slight destabilization of HOMO and stabilization of LUMO energy levels, due to the expansion of the π-conjugated system. The hypsochromic shift in **18c** can be ascribed to destabilization of LUMO energy level that comes from the introduction of an electron-donating dimethylamino group into the phenyl moiety. On the other hand, the introduction of an electron-withdrawing cyano group in **18d** brought about a large stabilization of the LUMO level to give the bathochromic shift.

The calculated energy levels of 5-[2-(9-julolidyl)ethenyl],

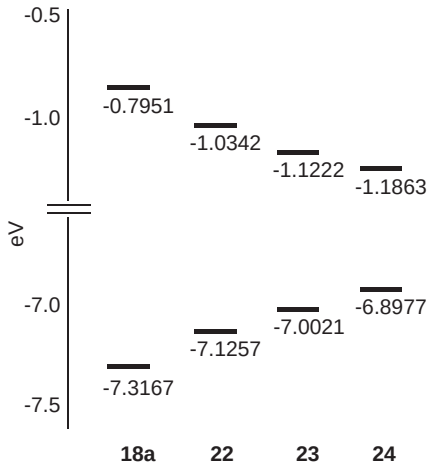


Fig. 6. Energy levels of **18a**, **22**, **23**, and **24**.

5-[4-(9-julolidyl)-1,3-butadienyl], 5-[6-(9-julolidyl)-1,3,5-hexatrienyl], and 5-[8-(9-julolidyl)-1,3,5,7-octatetraenyl] derivatives **18a**, **22**, **23**, and **24** are shown in Fig. 6. It is clear that expansion of the olefinic unit results in the stabilization of LUMO and destabilization of HOMO energy levels to cause the bathochromic shift.

Conclusion

We have synthesized a series of neutral fluorescent 2,3-dicyano-6*H*-1,4-diazepines. These compounds showed an intramolecular charge-transfer chromophoric system. Therefore, as stronger was the electron-donating ability at the 5-(2-arylethenyl) moiety, the λ_{max} and F_{max} could show more bathochromic shift. The expansion of π-conjugated system caused bathochromic shifts in λ_{max} and F_{max} because of destabilization of HOMO and stabilization of LUMO energy levels. 5-(2-Arylethenyl) derivative showed more intense fluorescence than the 5-aryl-7-(2-arylethenyl) and 5,7-bis(2-arylethenyl) derivatives. The fluorescence of 6-[2-(9-julolidyl)ethenyl] derivative was most intense among the 5-(2-arylethenyl) derivatives. The 5-[6-(9-julolidyl)-1,3,5-hexatrienyl] and 5-[8-(9-julolidyl)-1,3,5,7-octatetraenyl] derivatives showed the F_{max} in the near-infrared region at 780 and 842 nm, respectively.

Experimental

Instruments. Melting points were measured with a Yanagimoto MP-S2 micro-melting-point apparatus. EIMS spectra were recorded on a Shimadzu QP-1000 spectrometer. NMR spectra were obtained by a Varian Inova 400 spectrometer. Elemental analysis was performed with a Yanaco MT-6 CHN corder. UV–vis absorption and fluorescence spectra were taken on Hitachi U-3500 and F-4500 spectrophotometers, respectively.

Materials. Diaminomaleonitrile (DAMN, **1**) and 9-ethyl-3-carbazolecarbaldehyde (**11**) were purchased from Sigma-Aldrich. Acetylacetone (**2a**), 1-phenyl-1,3-butanedione (**2b**), benzaldehyde (**5**), 4-chlorobenzaldehyde (**6**), 4-(diethylamino)benzaldehyde (**7**), 2-thiophenecarbaldehyde (**9**), 2-furaldehyde (**10**) were purchased from Tokyo Kasei Co., Ltd. 4-(Dimethylamino)benzoylacetone (**2c**),[14] 4-(cyanobenzoyl)acetone (**2d**),[14] 2,3-dicyano-5,7-dimethyl-6*H*-1,4-diazepine (**4a**),[15] 2,3-dicyano-7-methyl-5-phenyl-6*H*-1,4-diazepine (**4b**),[16] 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizine-9-carbaldehyde (**8**),[17] 3-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizin-9-yl)propenal (**12**),[18] 5-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)-2,4-pentadienal (**13**),[18] and 7-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolinin-9-yl)-2,4,6-heptatrienal (**14**)[18] were prepared as described in the literature.

Synthesis of 5-Aryl-2,3-dicyano-7-methyl-6*H*-diazepines 4c and 4d. To a benzene solution (20 cm^3) of DAMN **1** (1.08 g, 10 mmol) were added oxalic acid (50 mg) and an aroylacetone **2c** or **2d** (10 mmol). The mixture was refluxed for 10 h in a system equipped with a Dean–Stark trap. After the solvent was removed, the product was isolated by silica gel column chromatography (dichloromethane/ethyl acetate = 10/1). The open-ring intermediates **3c** and **3d** were refluxed again in the presence of diphosphorus pentaoxide (500 mg) in ethanol (20 cm^3) for 13 h. After the reaction was completed, the solvent was evaporated. The residual brown syrup was treated with water and extracted with chloroform. After evaporation of the solvent in vacuo, the product was isolated by silica gel column chromatography (dichloromethane/ethyl acetate = 20/1) and recrystallized from benzene. The physical and spectral data are shown below.

2,3-Dicyano-5-[4-(dimethylamino)phenyl]-7-methyl-6*H*-1,4-diazepine (4c): Yield 67%; mp 204–205 °C; ^{1}H NMR ($CDCl_3$) δ 1.81 (br s, 1H), 2.14 (s, 3H), 3.11 (s, 6H), 4.89 (br s, 1H), 6.70 (d, J = 7.3 Hz, 2H), 7.89 (d, J = 7.3 Hz, 2H); EIMS (70 eV) m/z (rel intensity) (M^+, 93), 276 (42), 146 (100), 145 (44), 77 (34).

2,3-Dicyano-5-(4-cyanophenyl)-7-methyl-6*H*-1,4-diazepine (4d): Yield 27%; ^{1}H NMR ($CDCl_3$) δ 1.94 (br s, 1H), 2.26 (s, 3H), 5.03 (br s, 1H), 7.83 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H). This product was used without further purification.

Reaction of 2,3-Dicyano-6*H*-1,4-diazepines 4 with Aldehydes 5–14. To a benzene solution (15 cm^3) of **4** (1 mmol) were added piperidine (a few drops) and aldehydes **5**–**14** (1 mmol). The mixture was stirred (**15**: 50 °C to reflux for 3 d; **16**: 70 °C for 10 h; **17**, **18a**, **18′a**, **21**: reflux for 6 h; **18b**: reflux for 8 h; **18c**: reflux for 40 h; **18d**: 50 °C to reflux for 28 h; **19**, **20**: 50 °C for 24 h; **22**, **23**, **24**: 50 °C for 20 h). After the reaction was completed, the solvent was removed. The product was isolated by silica gel column chromatography (**15**, **16**, **17**, **18a**, **19**, **20**, **21**, **22**, **23**, **24**: toluene/ethyl acetate = 15/1; **18′a**, **18b**, **18c**, **18d**: dichloromethane/ethyl acetate = 20/1) and recrystallized from benzene. The physical and spectral data are shown below.

2,3-Dicyano-5-methyl-7-styryl-6*H*-1,4-diazepine (15): Mp 177–179 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.82 (br s, 1H), 2.27 (s, 3H), 4.69 (br s, 1H), 6.93 (d, J = 16.3 Hz, 1H), 7.44–7.45 (m, 3H), 7.53 (d, J = 16.3 Hz, 1H), 7.58–7.59 (m, 2H); EIMS (70 eV) m/z (rel intensity) 260 (M^+, 43), 259 (100), 258 (55), 219 (45), 218 (43), 217 (37), 128 (50), 77 (35), 51 (42). Found: C, 73.53; H, 4.83; N, 21.54%. Calcd for $C_{16}H_{12}N_4$: C, 73.83; H, 4.65; N, 21.52%.

2,3-Dicyano-5,7-distyryl-6*H*-1,4-diazepine (15′): Mp 276–278 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.87 (br s, 1H), 4.99 (br s, 1H), 6.89 (d, J = 16.1 Hz, 2H), 7.41–7.42 (m, 6H), 7.54–7.56 (m, 4H), 7.61 (d, J = 16.1 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 348 (M^+, 76), 347 (100), 129 (40), 128 (91), 127 (53), 77 (35), 51 (32).

5-(4-Chlorostyryl)-2,3-dicyano-7-methyl-6*H*-1,4-diazepine (16): Mp 185–187 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.83 (br s, 1H), 2.27 (s, 3H), 4.66 (br s, 1H), 6.88 (d, J = 16.2 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 16.2 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 296 (M^+ + 2, 18), 294 (M^+, 52), 293 (100), 253 (36), 128 (62), 127 (38). Found: C, 65.16; H, 3.85; N, 19.15%. Calcd for $C_{16}H_{11}ClN_4$: C, 65.20; H, 3.76; N, 19.01%.

5,7-Bis(4-chlorostyryl)-2,3-dicyano-6*H*-1,4-diazepine (16′): Mp 267–269 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.85 (br s, 1H), 4.85 (br s, 1H), 6.83 (d, J = 16.1 Hz, 2H), 7.39 (d, J = 8.7 Hz, 4H), 7.47 (d, J = 8.7 Hz, 4H), 7.54 (d, J = 16.1 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 420 (M^+ + 4, 13), 418 (M^+ + 2, 64), 417 (88), 416 (M^+, 89), 415 (85), 128 (100).

2,3-Dicyano-5-[4-(diethylamino)styryl]-7-methyl-6*H*-1,4-diazepine (17): Mp 222–224 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.21 (t, J = 7.2 Hz, 6H), 1.59 (s, 3H), 1.83 (br s, 1H), 3.43 (q, J = 7.2 Hz, 4H), 4.57 (br s, 1H), 6.67 (d, J = 15.9 Hz, 1H), 6.68 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 15.9 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 331 (M^+, 57), 317 (85), 316 (100). Found: C, 72.52; H, 6.53; N, 21.38%. Calcd for $C_{20}H_{21}N_5$: C, 72.48; H, 6.39; N, 21.13%.

2,3-Dicyano-5-methyl-7-[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]-6*H*-1,4-diazepine (18a): Mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 1H), 1.96 (quin, J = 6.0 Hz, 4H), 2.18 (s, 3H), 2.74 (t, J = 6.0 Hz, 4H), 3.29 (t, J = 6.0 Hz, 4H), 4.51 (br s, 1H), 6.61 (d, J = 15.9 Hz, 1H), 7.04 (s, 2H), 7.35 (d, J = 15.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) 21.4, 25.7, 27.7, 44.2, 50.1, 115.4, 115.7, 117.9, 120.8, 121.1, 121.4, 124.6, 128.4, 146.2, 146.6, 149.9, 155.4; EIMS (70 eV) m/z (rel intensity) 355 (M^+, 100), 354 (32), 303 (20); IR (KBr) 2217 cm^{-1} (CN). Found: C, 73.85; H, 6.13; N, 19.44%. Calcd for $C_{22}H_{21}N_5$: C, 74.34; H, 5.96; N, 19.70%.

2,3-Dicyano-5,7-bis[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizin-9-yl)ethenyl]-6*H*-1,4-diazepine (18′a): Mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 1H), 1.95 (quin, J = 6.0 Hz, 8H), 2.71 (t, J = 6.0 Hz, 8H), 3.26 (t, J = 6.0 Hz, 8H), 4.76 (br s, 1H), 6.58 (d, J = 15.8 Hz, 2H), 6.98 (s, 4H), 7.36 (d, J = 15.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) 21.5, 27.8, 38.9, 50.2, 116.6, 118.3, 121.2, 121.6, 122.5, 128.2, 144.7, 145.8, 151.5; EIMS (70 eV) m/z (rel intensity) 538 (M^+, 14), 355 (21), 186 (100); IR (KBr) 2220 cm^{-1} (CN). Found: C, 77.67; H, 6.50; N, 15.53%. Calcd for $C_{35}H_{34}N_6$: C, 78.04; H, 6.36; N, 15.60%.

2,3-Dicyano-5-phenyl-7-[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]-6*H*-1,4-diazepine (18b): Mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (br, 1H), 1.93 (quin, J = 6.0 Hz, 4H), 2.70 (t, J = 6.0 Hz, 4H), 3.26 (t, J = 6.0 Hz, 4H), 5.23 (br, 1H), 6.53 (d, J = 15.6 Hz, 1H), 6.95 (s, 2H), 7.42 (d, J = 15.6 Hz, 1H), 7.44–7.52 (m, 3H), 7.96–7.99 (m, 2H); EIMS (70 eV) m/z (rel intensity) 417 (M^+, 100), 416 (39), 186 (58). Found: C, 77.45; H, 5.73; N, 16.46%. Calcd for $C_{27}H_{23}N_5$: C, 77.67; H, 5.55; N, 16.77%.

2,3-Dicyano-5-[4-(dimethylamino)phenyl]-7-[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]-6*H*-1,4-diazepine (18c): Mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 1.82 (br, 1H), 1.94 (quin, J = 6.0 Hz, 4H), 2.71 (t, J = 6.0 Hz, 4H), 3.06 (s, 6H), 3.24 (t, J = 6.0 Hz, 4H), 5.14 (br, 1H), 6.54 (d, J = 15.8 Hz, 1H), 6.65 (dd, J = 7.1, 2.1 Hz, 2H), 6.95 (s, 2H), 7.35 (d, J = 15.8 Hz, 1H), 7.89 (dd, J = 7.1, 2.1 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 460 (M^+, 41), 224 (16), 196 (26), 186 (100). Found: C, 75.41; H, 6.22; N, 17.90%. Calcd for $C_{29}H_{28}N_6$: C, 75.63; H, 6.13; N, 18.25%.

2,3-Dicyano-5-(4-cyanophenyl)-7-[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]-quinolizin-9-yl)ethenyl]-6*H*-1,4-diazepine (18d): Mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 1.73 (br s, 1H), 1.95 (quin, J = 6.0 Hz, 4H), 2.72 (t, J = 6.0 Hz, 4H), 3.29 (t, J = 6.0 Hz, 4H), 5.17 (br s, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.97 (s, 2H), 7.47 (d, J = 15.6 Hz, 1H), 7.76 (dd, J = 8.7, 1.8 Hz, 2H), 8.09 (dd, J = 8.7, 1.8 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 442 (M^+, 100), 221 (32), 218 (50), 186 (80), 128 (35). Found: C, 75.67; H, 5.23; N, 18.64%. Calcd for $C_{28}H_{22}N_6$: C, 76.00; H, 5.01; N, 18.99%.

2,3-Dicyano-5-methyl-7-[2-(2-thienyl)ethenyl]-6*H*-1,4-diazepine (19): Mp 190–192 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.84 (br s, 1H), 2.27 (s, 3H), 4.57 (br s, 1H), 6.67 (d, J = 15.7 Hz, 1H), 7.13 (dd, J = 4.7, 3.6 Hz, 1H), 7.38 (d, J = 3.6 Hz, 1H), 7.49 (d, J = 4.7 Hz, 1H), 7.68 (d, J = 15.7 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 266 (M^+, 62), 265 (100), 225 (36), 135 (46), 91 (45). Found: C, 63.13; H, 3.90; N, 21.21%. Calcd for $C_{14}H_{10}N_4S$: C, 63.14; H, 3.78; N, 21.04%.

2,3-Dicyano-5,7-bis[2-(2-thienyl)ethenyl]-6*H*-1,4-diazepine (19′): Mp 287–289 °C (dec); ^{1}H NMR (DMSO-d_6) δ 2.10 (br s, 1H), 5.23 (br s, 1H), 6.79 (d, J = 16.0 Hz, 2H), 7.19 (dd, J = 5.0, 3.6 Hz, 2H), 7.62 (d, J = 3.6 Hz, 2H), 7.80 (d, J = 5.0 Hz, 2H), 8.26 (d, J = 16.0 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 360 (M^+, 24), 359 (23), 135 (22), 91 (100).

2,3-Dicyano-5-[2-(2-furyl)ethenyl]-7-methyl-6*H*-1,4-diazepine (20): Mp 174–176 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.84 (br s, 1H), 2.26 (s, 3H), 4.55 (br s, 1H), 6.56 (dd, J = 3.4, 1.4 Hz, 1H), 7.33 (d, J = 15.8 Hz, 1H), 7.57 (d, J = 1.4 Hz, 1H), 7.73 (d, J = 15.8 Hz, 1H), 7.79 (d, J = 3.4 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 250 (M^+, 48), 209 (49), 180 (100), 179 (69), 91 (58), 65 (62), 63 (57), 51 (69). Found: C, 66.91; H, 4.15; N, 22.38%. Calcd for $C_{14}H_{10}N_4O$: C, 67.19; H, 4.03; N, 22.39%.

2,3-Dicyano-5,7-bis[2-(2-furyl)ethenyl]-6*H*-1,4-diazepine (20′): Mp 281–283 °C (dec); ^{1}H NMR (DMSO-d_6) δ 2.09 (br s, 1H), 5.24 (br s, 1H), 6.69 (dd, J = 3.2, 1.4 Hz, 2H), 6.75 (d, J = 16.1 Hz, 2H), 7.05 (d, J = 3.2 Hz, 2H), 7.89 (d, J = 16.1 Hz, 2H), 7.91 (d, J = 1.4 Hz, 2H); EIMS (70 eV) m/z (rel intensity) 328 (M^+, 65), 271 (38), 180 (72), 179 (47), 91 (95), 65 (100), 63 (47), 51 (55).

2,3-Dicyano-5-[2-(9-ethyl-3-carbazolyl)ethenyl]-7-methyl-6*H*-1,4-diazepine (21): Mp 222–224 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.47 (t, J = 7.3 Hz, 3H), 1.88 (br s, 1H), 2.29 (s, 3H), 4.41 (q, J = 7.3 Hz, 2H), 4.76 (br s, 1H), 6.99 (d, J = 16.0 Hz, 1H), 7.31 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 16.0 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.34 (s, 1H); EIMS (70 eV) m/z (rel intensity) 377 (M^+, 100), 376 (66), 362 (32), 57 (31). Found: C, 76.32; H, 5.28; N, 18.26%. Calcd for $C_{24}H_{19}N_5$: C, 76.37; H, 5.07; N, 18.55%.

2,3-Dicyano-5,7-bis[2-(9-ethyl-3-carbazolyl)ethenyl]-6*H*-1,4-diazepine (21′): Mp 275–277 °C (dec); ^{1}H NMR (DMSO-d_6) δ 1.21 (t, J = 7.1 Hz, 6H), 2.09 (br, 1H), 4.34 (q, J = 7.1 Hz, 4H), 5.47 (br, 1H), 7.17 (d, J = 16.5 Hz, 2H), 7.23 (t, J = 8.2 Hz, 2H), 7.47 (t, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 4H), 7.92 (d, J = 7.7 Hz, 2H), 8.16 (d, J = 7.7 Hz, 2H), 8.37 (d, J = 16.5 Hz, 2H), 8.66 (s, 2H); EIMS (70 eV) m/z (rel intensity) 582 (M^+, 3), 377 (22), 246 (51), 231 (100), 208 (48), 219 (21).

2,3-Dicyano-5-methyl-7-[4-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)-1,3-butadienyl]-6*H*-1,4-diazepine (22): Mp 220–223 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 1H), 1.96 (quin, J = 6.0 Hz, 4H), 2.21 (s, 3H), 2.74 (t, J = 6.0 Hz, 4H), 3.27 (t, J = 6.0 Hz, 4H), 4.50 (br s, 1H), 6.25 (d, J = 15.4 Hz, 1H), 6.72 (dd, J = 15.4, 11.0 Hz, 1H), 6.87 (d, J = 15.4 Hz, 1H), 6.96 (s, 2H), 7.35 (dd, J = 15.4, 11.0 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 381 (M^+, 100), 355 (44), 186 (39), 172 (30), 91 (31). Found: C, 75.32; H, 6.37; N, 18.04%. Calcd for $C_{24}H_{23}N_5$: C, 75.56; H, 6.08; N, 18.36%.

2,3-Dicyano-5-methyl-7-[6-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)-1,3,5-hexatrienyl]-6*H*-1,4-diazepine (23): Mp 217–220 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.80 (br s, 1H), 1.96

(quin, $J = 5.9$ Hz, 4H), 2.20 (s, 3H), 2.74 (t, $J = 5.9$ Hz, 4H), 3.23 (t, $J = 5.9$ Hz, 4H), 4.49 (br s, 1H), 6.25 (d, $J = 15.0$ Hz, 1H), 6.39 (dd, $J = 15.0$, 11.4 Hz, 1H), 6.67–6.69 (m, 2H), 6.81–6.87 (m, 1H), 6.92 (s, 2H), 7.23–7.29 (m, 1H); EIMS (70 eV) m/z (rel intensity) 407 (M^+, 60), 406 (46), 405 (100), 173 (44), 172 (30). Found: C, 76.32; H, 6.37; N, 17.04%. Calcd for $C_{26}H_{25}N_5$: C, 76.63; H, 6.18; N, 17.19%.

2,3-Dicyano-5-methyl-7-[8-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)-1,3,5,7-octatetraenyl]-6*H*-1,4-diazepine (24): Mp 218–220 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.78 (br, 1H), 1.96 (quin, $J = 6.0$ Hz, 4H), 2.20 (s, 3H), 2.73 (t, $J = 6.0$ Hz, 4H), 3.20 (t, $J = 6.0$ Hz, 4H), 4.47 (br, 1H), 6.26 (d, $J = 15.3$ Hz, 1H), 6.34–6.40 (m, 2H), 6.56–6.59 (m, 1H), 6.64–6.67 (m, 2H), 6.78 (dd, $J = 14.2$, 11.2 Hz, 1H), 6.90 (s, 2H), 7.24 (dd, $J = 15.3$, 11.2 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 433 (M^+, 42), 432 (81), 431 (100), 172 (48), 131 (49), 91 (84). Found: C, 77.34; H, 6.37; N, 15.87%. Calcd for $C_{28}H_{27}N_5$: C, 77.57; H, 6.28; N, 16.15%.

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