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New syntheses and spectral properties of diazepine fluorescent dyes with non-planar molecular structure

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Abstract

Two types of new diazepine fluorescent dyes were synthesized by the condensation of *N*-(4-substituted-4-oxo-2-buten-2-yl)diaminomaleonitrile and 2,3-dicyano-6H-1,4-diazepines with an arylaldehyde. Regioselective condensation reaction are observed and their reactivities are evaluated from their optimized molecular structures obtained by means of the ab initio molecular orbital calculation methods. Substituent effects of the donor moiety to absorption and fluorescent properties in solution were correlated with chromophoric systems with regard to the non-planar diazepine moiety. A strong intramolecular charge-transfer chromophoric system of dyes are confirmed and its large Stokes shift of over 100 nm resulted in emission of red fluorescence. These dyes are of current interest as a red light emitter for electroluminescence devices.

Keywords: 2,3-Dicyano-6H-1,4-diazepine; 2,3-Dicyano-5-hydroxy-4H,6H-1,4-diazepine; Diazepine fluorescent dye; New fluorescent chromophore; Non-planar chromophoric system; Red EL emitter

1. Introduction

Fluorescent chromophores have been generally known to have planar and rigid π-conjugation systems, and many fluorescent chromophores have rigid ring systems such as stilbene, coumarin, naphthalimide, perylene and rhodamine. We studied new fluorescent chromophores based on a pyrazine nucleus and new fluorescent dyes such as styrylpyrazines [1], 2,5-bis(dialkylamino)-3,6-dicyano pyrazines [2], pyrazinoheterocycles [3] and pyrazinophthalocyanines [4] were reported. 2,3-Dicyano-6H-1,4-diazepine and its precursor, *N*-(4-substituted-4-oxo-2-buten-2-yl)diaminomaleonitrile have been known to be synthesized from 1,3-dicarbonyl compounds and diaminomaleonitrile [5,6]. 1,4-Diazepine has a seven-membered ring and has a non-planar, non-conjugated ring system at the 6-methylene group. Isomerization of 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine to its enamine form, 2,3-dicyano-5,7-dimethyl-1H-1,4-diazepine, was confirmed by ^{1}H-NMR spectra [5].

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On the other hand, organic fluorescent materials are currently used for various application fields such as emitter for electroluminescence (EL) devices and copy-preventing inks and so on. In particular, fluorescent dye materials which emit longer wavelength fluorescence in the red light region are strongly expected for full color EL display.

In this paper, new dicyano-1,4-diazepine fluorescent dyes were synthesized by the condensation of 2,3-dicyano-6H-1,4-diazepine or its precursor with arylaldehydes. The regioselective condensation reactions were correlated with the reactivities of the active methylene group which are evaluated from the optimized molecular structures with regard to non-planar diazepine ring system. Calculations were conducted by ab initio methods. The chromophoric systems of these new dyes were studied from the substituent effects on their absorption and fluorescence spectra in solution.

2. Results and discussion

*2.1. Syntheses of new fluorescent dyes derived from 2,3-dicyano-6H-1,4-diazepines **4** or its precursor **3** with arylaldehyde*

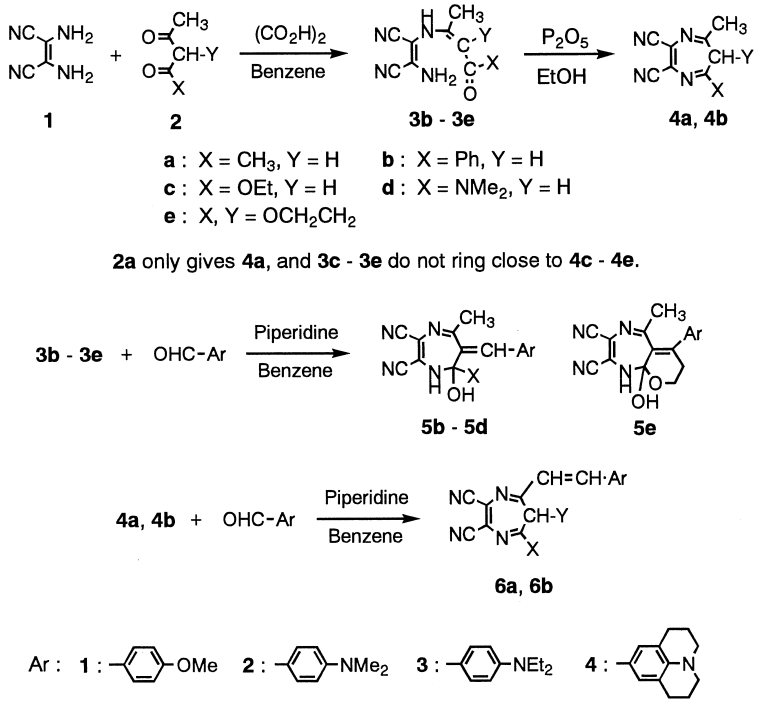
2,3-Dicyano-5,7-disubstituted-6H-1,4-diazpines **4** can be synthesized by the condensation of diaminomaleonitrile **1** with 1,3-dicarbonyl compounds **2** such as diacetyl [5], benzoylacetone and dibenzoylmethane [6]. In mild reaction conditions, the corresponding *N*-(4-substituted-4-oxo-2-buten-2-yl)diaminomaleonitrile **3** as a precursor of **4** could be synthesized in high yields [6]. Further condensation of **3** or **4** with an arylaldehyde gave the corresponding new dicyanodiazepine dyes **5** or **6**, respectively. The reaction of **3** with an arylaldehyde gave the ring-closed product **5**, 2,3-dicyano-5-hydroxy-5-substituted-7-methyl-6-(aryl) methylidene-4H-1,4-diazepine. On the other hand, the reaction of **4** with an arylaldehyde gave **6**, 2,3-dicyano-5-substituted-7-[2-(aryl)ethenyl]-6H-1,4-diazepine, in which the 7-methyl group of **4** was reacted. The reaction and structures of the products are summarized in Scheme 1.

The dicyanodiazepine moiety has a strong electron withdrawing ability, and the enamine of **3** or the 7-methyl group of **4** reacted easily with the formyl group of arylaldehydes to form a C–C double bond. It is very interesting that **3** consequently reacted with the arylaldehyde at the 6-position of the diazepine ring but **4** reacted at the 7-methyl group. The structures of the products were confirmed by their NMR spectra; dye **5** showed 7-methyl protons and a methylidene proton, but dye **6** showed trans-coupled ethenyl protons and geminal 6-methylene protons. Assignments of each proton are shown in the experimental section. Typical assignments for **5c**-**3** and **6a**-**3** by ^{1}H NMR are shown in Fig. 1.

The reaction of **3** or **4** with arylaldehyde was conducted in benzene under reflux by adding several drops of piperidine as a catalyst. The generated water was removed by a Dean–Stark trap during the reaction. The reaction products were isolated by column chromatography and were purified by recrystalization. In the reaction of **3e** with an arylaldehyde, the ring-expansion product **5e**, 2,3-dicyano-4a-hydroxy-9-methyl-8-(4-substituted phenyl)-4H,6H,7H-oxacyclohexano[2,3-e]-1,4-diazepine, was obtained. In the reaction, the sterically hindered seven-five ring system of **3e** was transformed to give the seven-six ring system of **5e**. The structural assignment of **5e** was conducted by mass spectra, elemental analysis, and ^{1}H and ^{13}C NMR spectra in which the 5-methyl group was observed and the methylidene proton was absent. The ^{13}C NMR data also confirm the structure of **5e** as shown in the experimental section. The regioselective condensations between **3** or **4** and arylaldehydes are proposed to be affected by the electronic and steric effects of the 5-substituent, but only one product, **5** from **3** or **6** from **4**, were isolated from each reaction.

*2.2. Optimized molecular structures of **3** and **4** by ab initio calculation method*

Regioselective condensations were observed to give **5** from **3**, and **6** from **4**. The differences in their reactivity are proposed to cause the stability of the enamine as a reactant in the case of **3**, and the planarity of the reaction site conjugated with the 2,3-dicyanodiazepine moiety as a strong acceptor in the case of **4**. The optimized molecular



Scheme 1.

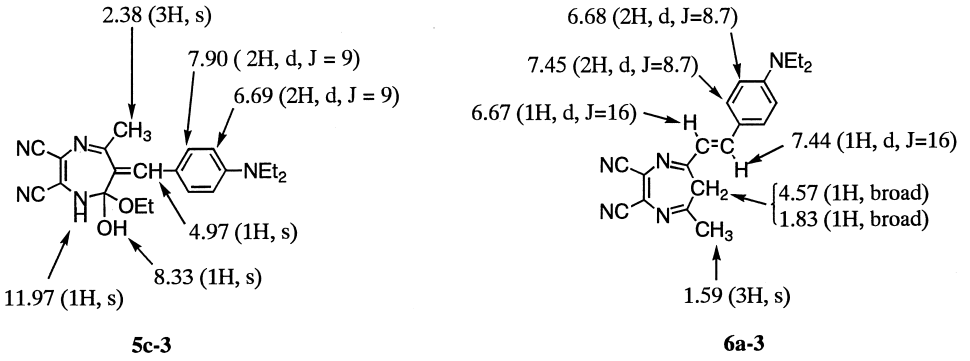


Fig. 1. Structural assignments of typical protons in **5c-3** and **6a-3** by ^{1}H NMR.

structure for *N*-(4-phenyl-4-oxo-2-buten-2-yl)-diaminomaleonitrile **3b** (for exemplified **3**) and 2,3-dicyano-6H-1,4-diazepine **4-H** (for exemplified **4**) were calculated by the ab initio method with RHF (Restricted Hartree-Fock) 3-21G* basis sets. The results are summarized in Fig. 2. In the case of **3b**, the enamine moiety is further conjugated with the benzoyl group keeping the planar conjugation system, but the diaminomaleonitrile residue did not conjugate with the enamine moiety. These results indicate that the condensation with arylaldehyde proceed at the methine site of the enamine as a strong nucleophile, and further ring-closure reaction between the amino group and the carbonyl group bonded with the sp^3 carbon (substituted methyl group) in the intermediate adduct process to give **5**. On the other hand, the 6-methylene group of **4-H** exists in a non-planar

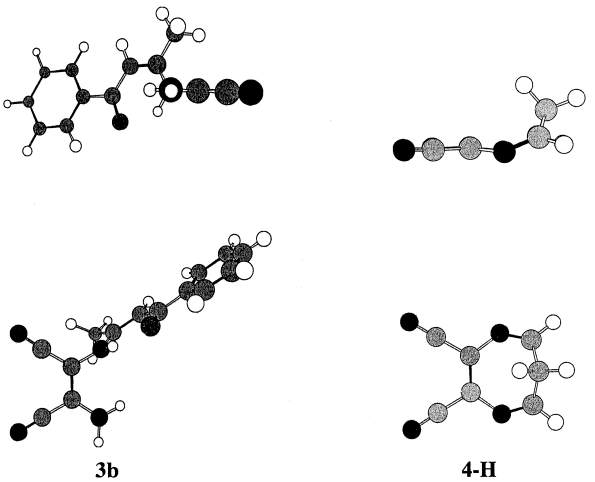
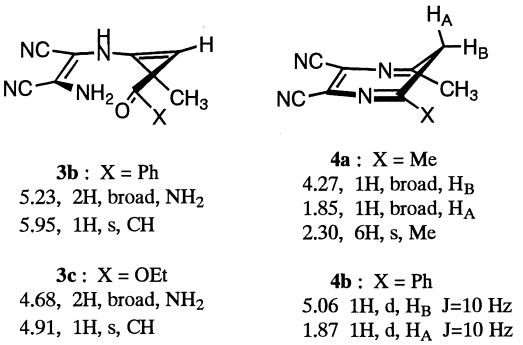


Fig. 2. The optimized molecular structures of **3b** and **4-H** calculated by the ab initio (RHF 3-21G*) method. The enamine moiety conjugates with the benzoyl group in **3b**, and the 6-methylene exists in non-polar site deviated largely from π-conjugation system in **4-H**.

site deviated largely from the dicyanodiazepine π-conjugated moiety (dihedral angle between 2,3- and 6,7-planes is 33.5°) of the molecule, and the methylene group cannot be incorporated with the enamine, but 5- or 7-hydrogens (methyl group in **4**) exist in a planar site and it can be conjugated with the azepine moiety. As a result, the reaction proceeds at the 7-methyl group of **4** to give **6**.

These differences in the calculation results are supported by the ^{1}H NMR spectra with respect to the 6-methylene protons in **4** (Fig. 3). The 6-methylene protons are observed as the two separated peaks around 4.3–5.0 ppm and 1.9 ppm with geminal coupling of 10 Hz in **4b**. The 5- and 7-methyl groups of **4a** exist in the same environment and are observed as a singlet of 6H at 2.30 ppm. From these results, each of the 6-methylene protons in **4** orients in a different manner; H_A orients toward the top of π-plane and is strongly shielded by the dicyanodiazepine π-conjugation moiety, and H_B orients outside the π-plane is deshielded.

Compound **3** has tautomeric and isomeric structures 3A–3D (Fig. 4). The pairs of A and B or C and D are azomethine/enamine tautomerism. The pairs of A and C or B and D are the ring-open/ring-closed structural isomers. The structure of **3** was confirmed by ^{1}H- and ^{13}C NMR together with ^{1}H–^{13}C two-dimensional NMR spectra. The



3b : X = Ph
5.23, 2H, broad, NH_2
5.95, 1H, s, CH

3c : X = OEt
4.68, 2H, broad, NH_2
4.91, 1H, s, CH

4a : X = Me
4.27, 1H, broad, H_B
1.85, 1H, broad, H_A
2.30, 6H, s, Me

4b : X = Ph
5.06 1H, d, H_B J=10 Hz
1.87 1H, d, H_A J=10 Hz

Fig. 3. Comparison of NMR spectra between **3** and **4** with respect to the ring-open enamine structure of **3** and the 6-methylene protons of **4**.

NMR results of *N*-(1,3-diphenyl-3-oxo-1-propen-1-yl)diaminomaleonitrile (known in the literature [6]) in d_6-DMSO indicates that the two protons observed at 7.82 ppm does not connected to carbon and are confirmed as the amino protons. The imino proton (1H, 11.45 ppm) and the amino protons are removed by adding a drop of D_2O. From these results, the structure of **3** was identified as 3B (cf. experimental section).

The calculated heats of formation of **3b** by the ab initio method for 3A and 3B are −825.1288982 H (Hamiltonian unit = 627.5 kcal/mol) and −825.1459949 H, respectively, and 3B is much more stable than 3A in 10.73 kcal/mol. The opti-

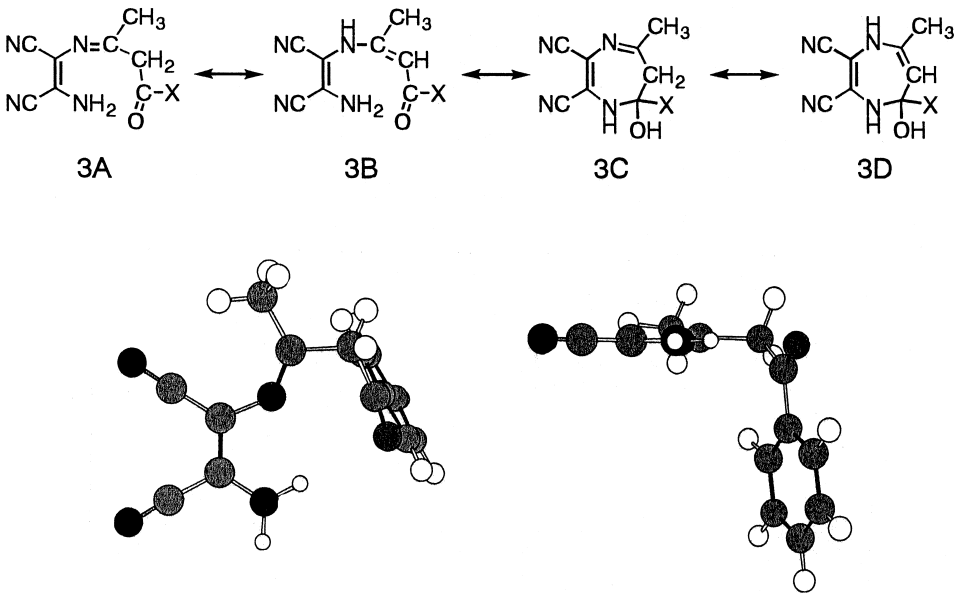


Fig. 4. Tautomeric and structural isomers of **3**, and the optimized molecular structure of 3A (X = Ph) by the ab initio (RHF 3-21G*) method.

mized molecular structure of 3A (in the case of **3b**) shows that the planar π-conjugation was observed through the amino group to the azomethine group, while the other part of the benzoyl methyl moiety twisted almost perpendicularly to the azomethine group (Fig. 4). From these calculation results, the ab initio method is valuable to evaluate the optimized molecular structure and the stability of the isomers especially as they have some energy differences between the configuration isomers and the structural isomers.

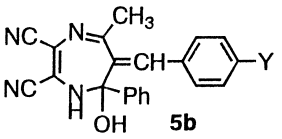
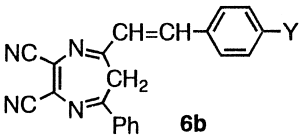
As a result, regioselective reactions to give **5** and **6** are well explained from the optimized molecular structures of **3** and **4**, respectively.

2.3. *Visible and fluorescent spectra of dyes 5 and 6*

Strong intramolecular charge-transfer chromophoric systems are observed for dyes **5** and **6**. The substituent effects of the donor group on their visible and fluorescent spectra are summarized in Table 1. The substituent Y acts as a strong donor and the dicyanodiazepine moiety acts as a strong acceptor. Both of the chromophoric systems are almost the same, except for the 4-amino-5-hydroxy moiety in **5** and the 4-imino moiety in **6**, and the π-conjugations through the donor (Y) to the 2,3-dicyanoethylene moiety produce strong donor-acceptor systems. As a result, differences in the visible and fluorescent spectra between **5** and **6** are mainly caused by the difference in the planarity of the π-conjugation; i.e. the degree of distortion in their diazepine ring systems.

Dye **5b-1** absorbs at 447 nm and emits at 512 nm. With increasing donor ability from the methoxy (**5b-1**) to the julolidine derivative (**5b-4**), their λ_{max} and F_{max} values show large bathochromic shifts to 555 nm ($\Delta\lambda = 108$ nm) and 613 nm ($\Delta F = 101$ nm), respectively. The Stokes shift (SS) values for **5b** are 53–65 nm and the ε_{max} values increase with increase of donor strength. Similar results are observed in the case of **6b**, but $\Delta\lambda$ and ΔF values are generally larger than those of the corresponding **5b**. As a result, **5b** absorbs in longer wavelength than **6b**, but the F_{max} value of **6b** produces bathochromic shifts comparable with those of **5b**. Dyes **6b-2–6b-4** emit red fluorescence over 600 nm in chloroform. The big difference in their SS values indicates that **6b** loose more energy in the excited state (bigger SS value) than that of **5b**. These observations are also confirmed by the ε values between the corresponding dyes **5b** and **6b**.

Table 1
Substituent effects of donor on their absorption and fluorescent spectra of **5b** and **6b**

	Dye No.	Y	λ_{max}[a]	$\Delta\lambda$	ε_{max}	F_{max}[a]	ΔF	SS[b]
 **5b**	**5b-1**	OCH_3	447	–	26,200	512	–	65
	5b-2	NMe_2	520	73	32,900	575	63	55
	5b-3	NEt_2	529	82	41,000	582	70	53
	5b-4	$N(C_2H_4)_2$[c]	555	108	33,700	613	101	58
 **6b**	**6b-1**	OCH_3	410	–	23,600	511	–	101
	6b-2	NMe_2	498	88	28,900	610	99	112
	6b-3	NEt_2	511	101	35,800	619	108	108
	6b-4	$N(C_2H_4)_2$[c]	541	131	31,700	649	138	108

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

Dye **5b** has bigger ε value than that of **6b** which indicates **5b** has a much more planar and rigid π-conjugation system than that of **6b**.

In conclusion, two types of new dicyanodiazepine fluorescent dyes are developed which have non-planar molecular structures with planar π-conjugation chromophoric systems. A new ring-expansion reaction to give **5e-3** from **3e** was also found.

3. Experimental

3.1. Materials and equipment

The ^{1}H- and ^{13}C-NMR spectra were taken on Varian Unity-plus 300 and Jeol JNM-A500 FT-NMR spectrometers in deuteriochloroform or deuteriodimethyl sulfoxide with tetramethylsilane as an internal standard. The mass spectra were recorded on a Shimadzu GCMS-QP5000 spectrometer. The uv/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 **1** is supplied from Nippon Soda Co., Ltd. 1-Dimethylaminobutane-1,3-dione and 3-acetyloxacyclopentane-2-one are supplied from Daicel Chemical Industries, Ltd. Other reagents are commercially available and are used without purification.

3.2. Syntheses of N-(4-substituted-4-oxo-2-buten-2-yl)diaminomaleonitrile *3a–e*

3.2.1. General procedure

A mixture of diaminomaleonitrile (**1**, 10 mmol), 1,3-dicarbonyl compound **2a**–**e** (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 to room temperature and the benzene was removed in vacuo. The residue was washed with water and filtered. The precipitate was purified by column chromatography on silica gel using chloroform as an eluent and then by recrystalization.

Compound **3a** was not isolated by this reaction but 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine **4a** was isolated exclusively.

3.2.2. N-(4-phenyl-4-oxo-2-buten-2-yl)-diaminomaleonitrile *3b [6]*

Yield: 82%, mp: 146–148 °C; δ_H ($CDCl_3$) 12.26 (1H, broad, NH), 7.83 (2H, *d*, phenyl protons), 7.47 (3H, *m*, phenyl protons), 5.95 (1H, *s*, =CH),

5.23 (2H, broad, NH_2), 2.07 (3H, *s*, CH_3); mass (*m*/*e*): 252 (M^+); Anal. calcd for $C_{14}H_{12}N_4O$: (C, 66.65, H, 4.79, N, 22.21%), found: (C, 65.94; H, 4.74; N, 23.13). The ring-closure structure of this compound was previously reported by us [7], but structural assignments by NMR was amended in this paper.

3.2.3. *N-(4-ethoxy-4-oxo-2-buten-2-yl)-diaminomaleonitrile* ***3c*** *[6]*

Yield: 58%, mp. 154–155 °C (152–153 °C [6]); δ_H ($CDCl_3$) 9.45 (1H, *s*, NH), 4.91 (1H, broad, =CH), 4.68 (2H, broad, NH_2), 4.13 (2H, *q*, $J=7.2$, CH_2), 2.06 (3H, *s*, CH_3), 1.28 (3H, *t*, $J=7.2$, CH_3); mass (*m*/*e*): 220 (M^+); Anal. calcd for $C_{10}H_{12}N_4O_2$ (C, 54.54; H, 5.49; N, 25.44%), found: (C, 54.33; H, 5.57; N, 25.46).

3.2.4. *N-(4-dimethylamino-4-oxo-2-buten-2-yl)-diaminomaleonitrile* ***3d***

Yield: 83%, mp: 149–151 °C; δ_H (d_6-DMSO) 10.34 (1H, *s*, NH), 7.40 (2H, *s*, NH_2), 5.17 (1H, *s*, =CH), 2.96 (3H, broad, NMe), 2.83 (3H, broad, NMe), 1.89 (3H, *s*, CH_3); δ_H ($CDCl_3$) 3.55 (2H, s, NH_2), 3.00 (3H, *s*, NMe), 2.93 (3H, *s*, NMe), 2.29 (3H, *s*, CH_3), NH and CH are not observed; mass (*m*/*e*): 219 (M^+); Anal. calcd for $C_{10}H_{13}N_5O$: (C, 54.78; H, 5.98; N 31.94%), found: (C, 54.66; H, 5.96; N, 31.92).

3.2.5. *N-[1-(1-oxa-2-oxocyclopentan-3-ylidene)-ethyl]diaminomaleonitrile* ***3e***

Yield: 75%, mp: 147–148 °C; δ_H ($CDCl_3$) 8.97 (1H, *s*, NH), 4.79 (2H, broad, NH_2), 4.39 (2H, *t*, $J=7.8$, OCH_2), 2.91 (2H, *t*, $J=7.8$, CH_2), 2.08 (3H, *d*, $J=0.9$, CH_3), δ_H (d_6-DMSO) 8.50 (1H, *s*, NH), 7.59 (2H, s, NH_2), 4.26 (2H, *t*, $J=7.8$, OCH_2), 2.83 (2H, *t*, $J=7.8$, CH_2), 1.90 (3H, *s*, CH_3), mass (*m*/*e*): 218 (M^+); Anal. calcd for $C_{10}H_{10}N_4O_2$: (C, 55.04; H, 4.62; N, 25.68%), found: (C, 54.80; H, 4.64; N, 25.69).

3.2.6. *N-(1,3-diphenyl-3-oxo-1-propen-1-yl)-diaminomaleonitrile [6]*

δ_H (d_6-DMSO) 11.455 (1H, *s*, NH), 8.029 (2H, *s*, $J=7.5$, phenyl protons), 7.822 (2H, *s*, NH_2), 7.53 (8H, *m*, phenyl protons), 6.346 (1H, *s*, =CH), ($CDCl_3$) 12.23 (1H, *s*, NH), 4.89 (2H, *s*, NH_2), δ_c (d_6-DMSO) 189.4 (C=O), 162.3 and 97.4 (NH–C=CH), 126.9 and 92.8 (NH_2–C=C), 135.0 and 132.2 (CN), 135.0, 132.2, 131.0, 127.7, 127.6 (phenyl). Two dimensional ^1H–^{13}C-NMR indicates that the two protons at 7.822 ppm did not connected to carbon and are confirmed as the amino protons, and existences of the amino group and the enamine form are confirmed.

3.3. *Syntheses of 2,3-dicyano-5-substituted-7-methyl-6H-1,4-diazepine* ***4a–e***

3.3.1. *General procedure*

A mixture of diaminomaleonitrile (**1**, 50 mmol), 1,3-dicarbonyl compounds **2a**–**e** (50 mmol) and phosphorus pentoxide (2.6 g) in ethanol (200 ml) was refluxed for 6 h in a flask. The mixture was cooled to room temperature and ethanol was evaporated until approximately 40 ml remained. The separated precipitate was filtered, dried and purified by column chromatography on silica gel using chloroform as an eluent and then by recrystalization. Compounds **4a** [5] and **4b** [6] are known.

3.3.2. *2,3-Dicyano-5,7-dimethyl-6H-1,4-diazepine* ***4a***

Mp: 199–200 °C; δ_H ($CDCl_3$) 4.27 (1H, broad, CH_2), 2.30 (6H, *s*, $2CH_3$), 1.85 (1H, broad, CH_2); mass (*m*/*e*): 172 (M^+).

3.3.3. *2,3-Dicyano-7-methyl-5-phenyl-6H-1,4-diazepine* ***4b***

Mp: 126–127 °C; δ_H ($CDCl_3$) 8.01 (2H, *d*, $J=8.2$, phenyl protons), 7.62 (1H, *m*, phenyl proton), 7.56 (2H, *m*, phenyl protons), 5.06 (1H, *d*, $J=10$, CH_2), 2.22 (3H, *s*, CH_3), 1.87 (1H, *d*, $J=10$, CH_2); mass (*m*/*e*): 234 (M^+).

Dehydration products **4c**, **4d** and **4e** were not obtained and **3c**–**3e** were obtained by this method, respectively.

3.4. *Syntheses of 2,3-dicyano-5-hydroxy-5-phenyl-7-methyl-6-[(4-substituted phenyl)methylidene]-4H-1,4-diazepine* ***5b***

3.4.1. *General procedure for* ***5***

A mixture of **3b** (5 mmol), arylaldehyde (5 mmol), and piperidine (several drops) in benzene

(50 ml) was refluxed in a flask equipped with a Dean–Stark trap to remove generated water. After 6 h, the mixture was cooled to room temperature, the benzene was evaporated and the separated precipitate was filtered. The product was isolated by column chromatography on silica gel using chloroform as an eluent to give **5b**.

3.4.2. 2,3-Dicyano-5-hydroxy-5-phenyl-7-methyl-6-[(4-methoxyphenyl)methylidene]-4H-1,4-diazepine ***5b-1***

Yield: 35%; mass (*m*/*e*): 370 (M^+).

3.4.3. 2,3-Dicyano-5-hydroxy-5-phenyl-7-methyl-6-[(4-dimethylaminophenyl)methylidene]-4H-1,4-diazepine ***5b-2***

Yield: 55%; mass (*m*/*e*): 383 (M^+); Anal. calcd for $C_{23}H_{21}N_5O$: (C, 72.04; H, 5.52; N, 18.27%), found: (C, 71.97; H, 5.58; N, 18.04).

3.4.4. 2,3-Dicyano-5-hydroxy-5-phenyl-7-methyl-6-[(4-diethylaminophenyl)methylidene]-4H-1,4-diazepine ***5b-3***

Yield: 42%; mp: 180–183 °C; δ_H ($CDCl_3$) 13.92 (1H, *s*, NH), 8.39 (1H, *s*, OH), 8.07 (2H, broad, phenyl protons), 7.97 (2H, *d*, $J=7$, phenyl protons), 7.51 (3H, *m*, $J=7$, phenyl protons), 6.74 (2H, *d*, $J=9$, phenyl protons), 6.09 (1H, *s*, CH), 3.49 (4H, *q*, $J=7.2$, CH_2), 2.54 (3H, *s*, CH_3), 1.25 (6H, *t*, $J=7.2$, CH_3); mass (*m*/*e*): 411 (M^+); Anal. calcd for $C_{25}H_{25}N_5O$: (C, 72.97; H, 6.12; N, 17.02%), found: (C, 72.47; H, 6.41; N, 16.59).

3.4.5. 2,3-Dicyano-5-hydroxy-5-phenyl-7-methyl-6-[(julolidin-9-yl)methylidene]-4H-1,4-diazepine ***5b-4***

Yield: 42%; mass (*m*/*e*): 435 (M^+).

3.4.6. 2,3-Dicyano-5-hydroxy-5-ethoxy-7-methyl-6-[(4-diethylaminophenyl)methylidene]-4H-1,4-diazepine ***5c-3***

Yield: 23%, mp: 164–166 °C; δ_H ($CDCl_3$) 11.97 (1H, *s*, NH), 8.33 (1H, *s*, OH), 7.90 (2H, *d*, $J=9.0$, phenyl protons), 6.69 (2H, *d*, $J=9.0$, phenyl protons), 4.97 (1H, *s*, CH), 4.25 (2H, *q*, $J=7.2$, CH_2), 3.46 (4H, *q*, $J=7.2$, $2CH_2$), 2.38 (3H, *s*, CH_3), 1.32 (3H, *t*, $J=7.2$, CH_3), 1.23 (6H, *t*, $J=7.2$, $2CH_3$); mass (*m*/*e*): 379 (M^+); uv: λ_{max} 499 nm (ε 45,800), F_{max} 544 nm; Anal. calcd for $C_{21}H_{25}N_5O_2$: (C, 66.47; H, 6.64; N, 18.46%), found: (C, 66.43; H, 6.54; N, 17.91).

3.4.7. 2,3-Dicyano-5-hydroxy-5-dimethylamino-7-methyl-6-[(4-diethylaminophenyl)methylidene]-4H-1,4-diazepine ***5d-3***

Yield: 25%, mp: 155–158 °C; δ_H ($CDCl_3$) 13.39 (1H, *s*, NH), 8.31 (1H, *s*, OH), 7.95 (2H, broad, phenyl protons), 6.67 (2H, *d*, $J=7.8$, phenyl protons), 5.17 (1H, *s*, CH), 3.44 (4H, *q*, $J=7.2$, CH_2), 3.06 (6H, *s*, NCH_3), 2.39 (3H, *s*, CH_3), 1.22 (6H, *t*, $J=7.2$, CH_3); mass (*m*/*e*): 378 (M^+); uv: λ_{max} 502 nm (ε 34,200), F_{max} 543 nm; Anal. calcd. for $C_{21}H_{26}N_6O$: (C, 66.64; H, 6.92; N, 22.21%), found: (C, 66.52; H, 6.97; N, 22.21).

3.4.8. 2,3-Dicyano-4a-hydroxy-9-methyl-8-(4-diethylaminophenyl)-4H,6H,7H-oxacyclohexano[2,3-e]-1,4-diazepine ***5e-3***

Yield: 40%, mp: 184–185 °C; δ_H ($CDCl_3$) 11.63 (1H, *s*, NH), 8.31 (1H, *s*, OH), 7.91 (2H, broad, phenyl protons), 6.72 (2H, *d*, $J=8$, phenyl protons), 4.41 (2H, *t*, CH_2), 3.44 (4H, *q*, $J=7$, CH_2), 3.00 (2H, *t*, CH_2), 2.43 (3H, s, CH_3), 1.22 (6H, *t*, $J=7$, CH_3); δ_c ($CDCl_3$) 172.9 (7-C), 160.5 (2′-C), 151.7 (4′-C), 146.5 (3-C), 122.2 (1′-C), 117.1 (CN), 114.7, 113.5, 112.3 (2-, 6- and olefinic-C), 111.5 (3′-C), 98.4 (5-C), 65.4 (OCH_2), 44.7 (NCH_2), 26.3 (OCH_2CH_2), 17.8 (7-Me), 12.6 (NCH_2Me); uv: λ_{max} 510 nm (ε 44,600), F_{max} 556 nm; mass (*m*/*e*): 377 (M^+); Anal. calcd for $C_{21}H_{23}N_5O_2$: (C, 66.82; H, 6.14; N, 18.56%), found: (C, 66.42; H, 6.33; N, 18.28).

3.5. Syntheses of 2,3-dicyano-5-methyl-7-[2-(4-diethylaminophenyl)ethenyl]-6H-1,4-diazepine ***6a-3***

3.5.1. General procedures for **6**

A mixture of **4a** (5 mmol), 4-diethylaminobenzaldehyde (5 mmol), and piperidine (several drops) in benzene (50 ml) was refluxed in a flask equipped with a Dean–Stark trap to remove generated water. After 6 h, the mixture was cooled to room temperature, the benzene was evaporated and the separated precipitate was filtered. The product was isolated by column chromatography on silica gel using chloroform as an eluent to give **6a-3**.

3.5.2. 2,3-Dicyano-5-methyl-7-[2-(4-diethylaminophenyl)ethenyl]-6H-1,4-diazepine ***6a-3***

Yield: 50%; mp: >300 °C; δ_H ($CDCl_3$) 7.45 (2H, *d*, *J*=8.7, phenyl protons), 7.44 (1H, *d*, *J*=15.9, CH), 6.68 (2H, *d*, *J*=8.7, phenyl protons), 6.67 (1H, *d*, *J*=15.9, CH), 4.57 (1H, broad, CH_2), 3.43 (4H, *q*, *J*=7.2, $2CH_2$), 1.83 (1H, broad, CH_2), 1.59 (3H, *s*, CH_3), 1.21 (6H, *t*, *J*=7.2, $2CH_3$); mass (*m*/*e*): 331 (M^+); uv: λ_{max} 490 nm (ε 40,400), F_{max} 589 nm; Anal. calcd for $C_{20}H_{21}N_5$: (C, 72.48; H, 6.39; N, 21.13%), found: (C, 72.63; H, 6.40; N, 20.41).

3.5.3. 2,3-Dicyano-5-phenyl-7-[2-(4-methoxyphenyl)-ethenyl]-6H-1,4-diazepine ***6b-1***

Yield: 30%; mp: 188–190 °C; mass (*m*/*e*): 352 (M^+); Anal. calcd for $C_{22}H_{16}N_4O$: (C, 74.98; H, 4.58; N, 15.90%), found: (C, 74.72; H, 4.90; N, 15.42).

3.5.4. 2,3-Dicyano-5-phenyl-7-[2-(4-dimethylaminophenyl)ethenyl]-6H-1,4-diazepine ***6b-2***

Yield: 38%; mp: 238–240 °C; mass (*m*/*e*): 365 (M^+); Anal. calcd for $C_{23}H_{19}N_5$: (C, 75.59; H, 5.24; N, 19.17%), found: (C, 75.00; H, 5.40; N, 18.95).

3.5.5. 2,3-Dicyano-5-phenyl-7-[2-(4-diethylaminophenyl)ethenyl]-6H-1,4-diazepine ***6b-3***

Yield: 33%; mp: 198–200 °C; δ_H ($CDCl_3$) 7.99 (2H, *d*, *J*=8.1, phenyl protons), 7.50 (3H, *m*, phenyl protons), 7.50 (1H, *d*, *J*=15.9, CH), 7.36 (2H, *d*, *J*=8.7, phenyl protons), 6.61 (2H, *d*, *J*=8.7, phenyl protons), 6.58 (1H, *d*, *J*=15.9, CH), 5.30 (1H, broad, CH_2), 3.40 (4H, *q*, *J*=7.2, $2CH_2$), 1.95 (1H, broad, CH_2), 1.19 (6H, *t*, *J*=7.2, $2CH_3$); mass (*m*/*e*): 393 (M^+); Anal. calcd for $C_{25}H_{23}N_5$: (C, 76.31; H, 5.89; N, 17.80%), found: (C, 75.78; H, 6.04; N, 17.27).

3.5.6. 2,3-Dicyano-5-phenyl-7-[2-(julolidin-9-yl)-ethenyl]-6H-1,4-diazepine ***6b-4***

Yield: 28%; mp: 246–248 °C; mass (*m*/*e*): 417 (M^+); Anal. calcd for $C_{27}H_{23}N_5$: (C, 77.67; H, 5.55; N, 16.78%), found: (C, 76.67; H, 5.60; N, 16.41).

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