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PREPARATION OF AZULENE SUBSTITUTED PYRAZINE AND QUINOXALINE DERIVATIVES

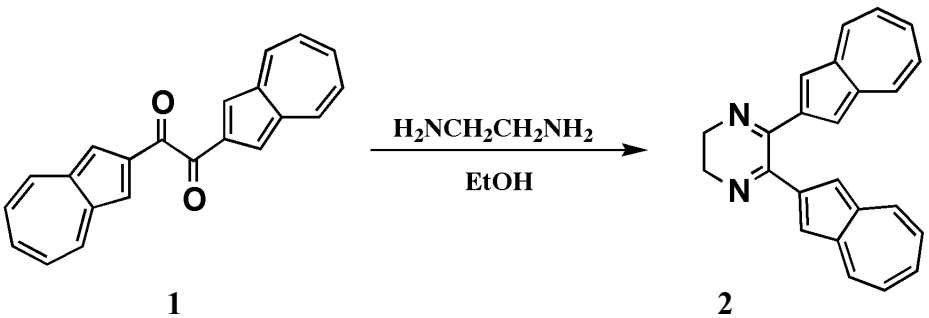
Nozomi Furuta, Takuo Mizutani, Akira Ohta, and Kunihide Fujimori*

Department of Chemistry, Faculty of Science, Shinshu University, Asahi Matsumoto 390-8621, Japan. E-mail: kfujimo@shinshu-u.ac.jp

Abstract – 2,3-Di(2-azulenyl)pyrazines and -quinoxalines were obtained by the reaction of di(2-azulenyl)ethanedione with diamines. Cyclodehydrogenation reaction of the pyrazine and quinoxaline derivatives with manganese dioxide afforded the corresponding azulene-fused quinoxaline and phenazine derivatives, respectively.

Azulene has attracted the interest of many research groups from the standpoint of synthetic and theoretical studies, due to its unusual properties.[1] On the other hand, heterocyclic compounds, pyrazines and quinoxalines, are of interest not only in their physical properties and chemical behavior, but also in their physiological activities and molecular electronics.[2] This paper describes the synthesis of azulene substituted pyrazine and quinoxaline derivatives.

One of the authors (K. Fujimori) has reported the facile synthetic method and reactivities of di(2-azulenyl)ethanedione (**1**).[3] Compound **1** afforded 2,3-di(2-azulenyl)-5,6-dihydropyrazine (**2**) by the reaction with ethylenediamine in good yield (Scheme 1). Oxidation of **2** with chloranil gave 2,3-di(2-azulenyl)pyrazine (**3**) in almost quantitative yield. Furthermore, compound **2** was readily converted into **3** on a column of basic alumina with toluene.

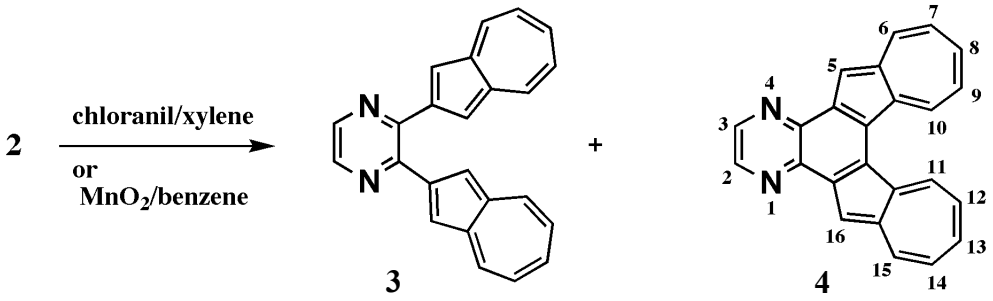


1 **2**

Scheme 1

This paper is dedicated to Professor Emeritus Keiichiro Fukumoto on the occasion of his 75th birthday.

On the other hand, the treatment of **2** with activated manganese dioxide afforded **3** and **4** in 41% and 20% yields, respectively (Scheme 2). Formation of **4** is ascribed to the oxidative cyclodehydrogenation reaction of **3**. Actually, the treatment of **3** with activated manganese dioxide gave **4** in 36% yield.

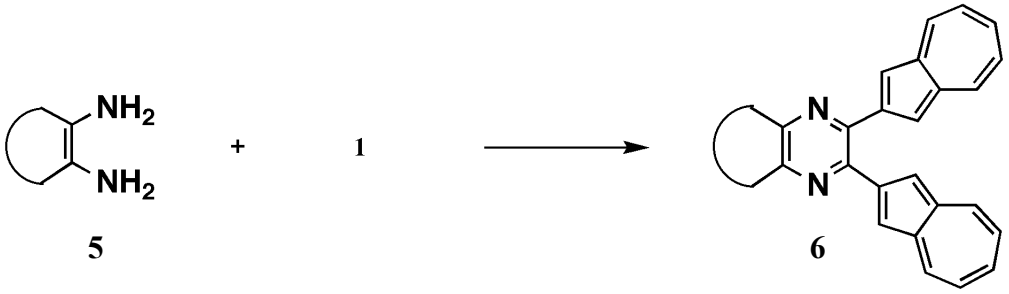


Scheme 2

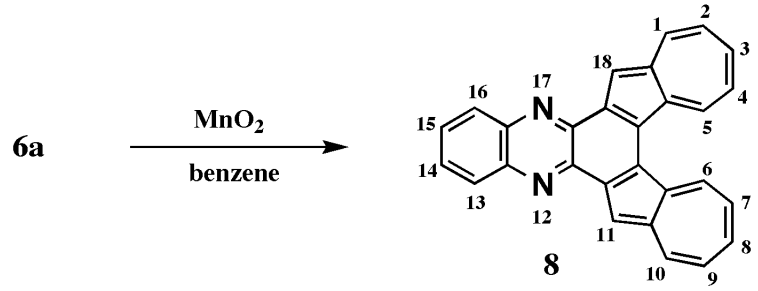
Table 1. Oxidation of compound **2**

entry	reaction condition	products (%)	
		3	**4**
1	MnO_2 (40 eq), dry benzene, r.t., 67 h	28	—
2	MnO_2 (20 eq), dry benzene, reflux, 20.5 h	41	20
3	chloranil (1 eq), dry xylene, reflux, 2 h	99	—

A reaction that characterizes compound **1** as an α-diketone is condensation reaction with *o*-phenylenediamines (**5a** - **g**) to give the corresponding quinoxaline derivatives (**6a** - **g**) (Scheme 3, Table 2). 2,3,7,8-Tetra(2-azulenyl)pyradino[2,3-*g*]quinoxaline (**7**) could not be obtained by the reaction of 6,7-diamino-2,3-di(2-azulenyl)quinoxaline (**6d**) with dione **1**. Cyclodehydrogenation reaction of **6a** with activated manganese dioxide afforded **8** in 20% yield (Scheme 4). These novel azulene fused quinoxaline derivatives (**4**, **8**) are stable, showing no decomposition even after several weeks at room temperature.

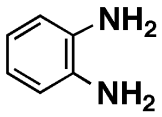
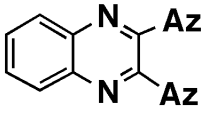
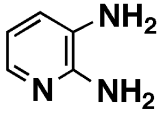
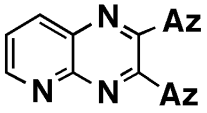
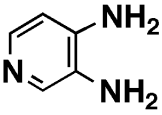
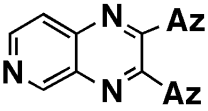
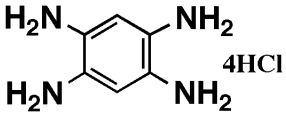
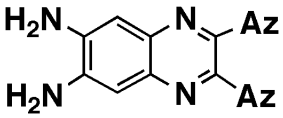
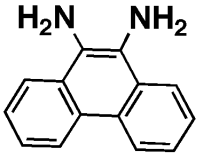
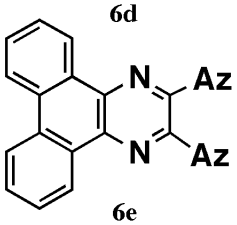
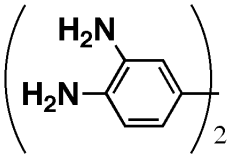
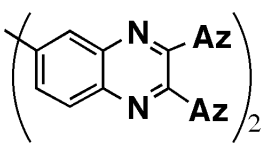
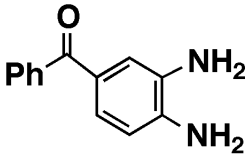
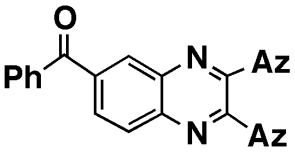


Scheme 3



Scheme 4

Table 2. Reaction of di(2-azulenyl)ethanedione (**1**) with *o*-phenylenediamines (**5**)

entry	*o*-phenylenediamines	reflux in EtOH times	products	yields (%)	crystals mp
1	 **5a**	40 min	 **6a**	78	dark blue needles mp 213-214 °C
2	 **5b**	20 h	 **6b**	97	dark blue needles mp 243-245 °C
3	 **5c**	26 h	 **6c**	87	dark blue needles mp 204-205 °C
4	 **5d**	1 h	 **6d**	94	brown solid mp 190-193 °C
5	 **5e**	21 h	 **6e**	75	yellowish green plates mp 275-277 °C
6	 **5f**	45 h	 **6f**	54	yellowish green powder mp > 300 °C
7	 **5g**	51 h	 **6g**	93	yellowish green crystals mp 221-222 °C

Az = 2-azulenyl

All the spectral data and elemental analyses supported the structure of the new compounds. The structure of **6a** was also confirmed by X-ray analysis (Figure 1). Single crystals of **4** or **8** suitable for X-ray analysis were not obtained. But the vicinal coupling constants on ^{1}H NMR allow us to estimate the degree of bond alternation in the seven-membered ring.[4] The coupling constants ($^3J_{HH}$) of **4**, **8** vary between 9.0-9.2 Hz across the formal C-C bonds and 10.0-10.1 Hz across the formal C=C bonds in the seven-membered ring. These values indicate the existence of some bond alternation in the seven-membered ring of **4**, **8**, although the degree is considerably smaller than that in benz[*a*]azulene.[4] The chemical shifts of 10-H, 11-H protons in compound **4** and those of 5-H, 6-H protons in compound **8** were observed at lower field than the corresponding protons of **3** or **6a** owing to anisotropic effect of neighboring azulene ring. UV-VIS spectra of **3**, **4**, **6a**, and **8** in dichloromethane show that the abosorption maxima in the visible region were significantly influenced by the ring closure at the 1,1'-positions of the two azulene rings.[3] The azulene-fused quinoxaline and phenazine derivatives **4**, **8** exhibited the longest wavelength absorption up to 815 nm and 777 nm, respectively.

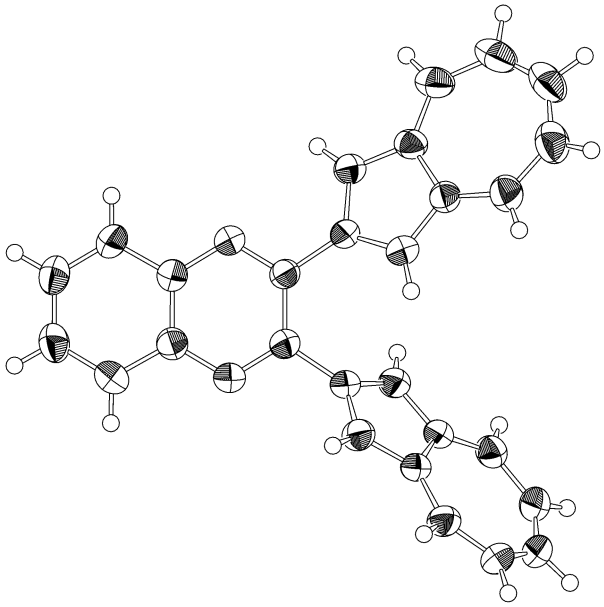


Figure 1. X-Ray molecular structure of **6a**.

EXPERIMENTAL

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Spectral data were obtained on the following instruments: ^{1}H-NMR: JEOL-JNM-LA300 (300 MHz), and -LA400 (400 MHz); ^{13}C-NMR; JEOL-JNM-LA300 (75.5 MHz), and –LA400 (100 MHz); IR: JEOL JIR-Diamond20; MS spectroscopy: Shimadzu GCMS-QP1000EX; UV-VIS: Shimadzu UV-260. Elemental analyses were performed on a Perkin-Elmer model 240.

2,3-Di(2-azulenyl)-5,6-dihydropyrazine (2). A mixture of di(2-azulenyl)ethanedione (**1**) (307 mg, 0.99 mmol) and ethylenediamine (0.1 mL) in EtOH (120 mL) was refluxed for 30 min. Reaction mixture was poured in water and extracted with $CHCl_3$. The dried organic layer was concentrated and the residue was purified by column chromatography on silica gel to afford **2** (263 mg, 79%) as dark blue needles, mp 176-178 °C and 2,3-di(2-azulenyl)pyradine (**3**) (51 mg, 16%) as dark bluish green plates, mp 189-190 °C. **2**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 3.18 (4H, s, H-5, 6), 7.08 (4H, t, J = 9.7 Hz, *Az* -5', 7', 5", 7"), 7.39 (4H, s, *Az* -1', 3', 1", 3"), 7.53 (2H, t, J = 9.7 Hz, *Az* - 6', 6'), 8.18 (4H, d, J = 9.7 Hz, *Az* -4', 8', 4", 8"). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 46.1, 118.1, 123.8, 138.6, 138.7, 140.0, 145.8, 158.6. IR (KBr): 3079, 2937, 1552, 1191, 826 cm^{-1}. MS: *m/z* (rel. int. %) 334 (M^+, 100), 306 (18), 252 (7), 127 (Az^+, 19). UV-VIS (CH_2Cl_2) λ_{max} (log ε): 221 (4.46), 242 (4.56), 283 (4.92), 300^{sh} (4.81), 340^{sh} (4.08), 365 (4.03), 603 (2.96), 635 (2.95), 698^{sh} (2.64). Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 85.99; H, 5.45; N, 8.31.

2,3-Di(2-azulenyl)pyrazine (3).

a) Oxidation using activated manganese dioxide, Method 1. A mixture of **2** (29 mg, 0.09 mmol) and activated manganese dioxide (155 mg, 1.79 mmol) in benzene (10 mL) was stirred at rt for 41 h. To a reaction mixture was added fresh activated manganese dioxide (160 mg, 1.85 mmol) and then the mixture was stirred for 26 h. From the reaction mixture, excess manganese dioxide was removed by filtration. The organic layer was concentrated and the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **3** (8 mg, 28%) as dark bluish green plates, mp 189-190 °C. **Method 2.** A mixture of **2** (51 mg, 0.15 mmol) and activated manganese dioxide (260 mg, 2.99 mmol) in benzene (17 mL) was refluxed for 20 h. After workup, the residue was purified by column chromatography on silica gel with chloroform to give **3** (21 mg, 41%) and diazuleno[2,1-*f*:1,2-*h*]quinoxaline (**4**) (10 mg, 20%). **3**: ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.10 (4H, t, J = 9.8 Hz, *Az* -5', 7', 5", 7"), 7.53 (2H, t, J = 9.8 Hz, *Az* -6', 6"), 7.53 (4H, s, *Az* -1', 3', 1", 3"), 8.20 (4H, d, J = 9.8 Hz, *Az* -4', 8', 4", 8"), 8.62 (2H, s, H-5,6). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 118.4, 123.5, 137.8, 137.9, 140.2, 142.0, 147.5, 150.1. IR (KBr): 3052, 1573, 1142, 818 cm^{-1}. MS: *m/z* (rel. int. %) 332 (M^+, 79), 331 (100), 254 (10), 127 (Az^+, 6). UV-VIS (CH_2Cl_2) λ_{max} (log ε): 278 (4.88), 320 (4.70), 391 (4.21), 595 (2.86), 635 (2.85), 698^{sh} (2.53). Anal. Calcd for $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43. Found: C, 86.55; H, 4.93; N, 8.37. **4**: Dark green needles; mp 198-199 °C; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.2-7.3 (4H, m, H-7, 9, 12, 14), 7.11 (2H, t, J =9.6 Hz, H-8, 13), 8.56 (2H, s, H-5, 16), 8.58 (2H, d, J =10.0 Hz, H-6, 15), 9.03 (2H, s, H-2, 3), 9.53 (2H, d, J =9.0 Hz, H-10, 11). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ: 115.1, 123.1, 123.2, 124.0, 135.6, 136.1, 138.9, 139.0, 139.1, 139.5, 141.4, 143.5. IR (KBr): 3054, 1571, 1213, 808 cm^{-1}. MS: *m/z* (rel. int. %) 330 (M^+, 100), 304 (7), 276 (5). UV-VIS (CH_2Cl_2) λ_{max} (log ε): 237 (4.46), 275 (4.73), 321 (4.60), 358^{sh} (4.41), 374 (4.45), 396^{sh} (4.41), 413 (4.49),

455 (4.06), 653 (3.05), 700^{sh} (2.98), 815^{sh} (2.61). Anal. Calcd for $C_{24}H_{14}N_2$: C, 87.25; H, 4.27; N, 8.48. Found: C, 87.25; H, 4.22; N, 8.59.

b) Oxidation using chloranil. A solution of **2** (51 mg, 0.15 mmol) and chloranil (37 mg, 0.15 mmol) in xylene (15 mL) was refluxed for 2 h. To the reaction mixture was added Et_2O (30 mL) and the organic layer was washed with 1% NaOH aqueous solution for three times, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with $CHCl_3$ to afford **3** (50 mg, 99%) as dark green plates (mp 189-190 °C). The IR spectrum was identical with that of the sample prepared by means of Method 1, 2 and the mixed melting point with the sample was not depressed.

Diazuleno[2,1-*f*:1,2-*h*]quinoxaline (4). A mixture of **3** (54 mg, 0.16 mmol) and activated manganese dioxide (267 mg, 3.07 mmol) in toluene (17 mL) was refluxed for 22 h. To a reaction mixture was added fresh activated manganese dioxide (270 mg, 3.11 mmol) and then the mixture was stirred for 19 h. From the reaction mixture, excess manganese dioxide was removed by filtration. The organic layer was concentrated and the residue was purified by column chromatography on silica gel with $CHCl_3$ to give **4** (18 mg, 36%) as dark green needles, mp 198-199 °C. The IR spectrum was identical with that of the sample prepared by the reaction of **2** with activated manganese dioxide and the mixed melting point with the sample was not depressed.

2,3-Di(2-azulenyl)quinoxaline (6a). A mixture of 1,2-di(2-azulenyl)ethanedione (**1**) (100 mg, 0.33 mmol), *o*-phenylenediamine (**5a**) (44 mg, 0.05 mmol), and molecular sieve 3Å in dry EtOH (40 mL) was refluxed for 40 min. After work up, the residue was purified by column chromatography on silica gel with benzene to afford **6a** as dark blue needles (mp 213-214 °C, from EtOH) in 78% yield. ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.11 (4H, t, J = 9.9 Hz, *Az* -5', 7', 5", 7"), 7.54 (2H, dd, J = 9.9 Hz, *Az* -6', 6"), 7.57 (4H, s, *Az* -1', 3', 1", 3"), 7.7-7.8 (2H, m, H - 6, 7), 8.1-8.2 (2H, m, H - 5, 8), 8.23 (4H, d, J = 9.9 Hz, *Az* -4', 8', 4", 8"). IR (KBr): 3047, 3018, 1568, 823 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 245 (4.53), 292 (4.92), 316^{sh} (4.73), 384 (4.38), 600 (2.90), 637 (2.89), 700 (2.56). Anal. Calcd for $C_{28}H_{18}N_2$: C, 87.93; H, 4.74; N, 7.32. Found: C, 87.86; H, 4.91; N, 7.21.

2,3-Di(2-azulenyl)-5-azaquinoxaline (6b). A mixture of **1** (50 mg, 0.16 mmol) and 2,3-diaminopyridine (**5b**) (27 mg, 0.25 mmol) in dry EtOH was refluxed for 20 h. The reaction mixture was concentrated to leave a residue. The residue was purified by column chromatography on silica gel with AcOEt-hexane (1:1) to give **6b** (60 mg, 97%) as dark blue needles (mp 243-245 °C). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.08 (2H, t, J = 9.9 Hz, *Az* -5', 7'), 7.15 (2H, t, J = 9.9 Hz, *Az*-5", 7"), 7.53 (1H, t, J = 9.9 Hz, *Az* -6'), 7.59

(1H, t, *J* = 9.9 Hz, *Az* -6"), 7.63 (2H, s, *Az* -1', 3'), 7.6-7.7 (1H, m, H-7), 7.67 (2H, s, *Az* -1", 3"), 8.20 (2H, d, *J* = 9.9 Hz, *Az* -4', 8'), 8.27 (2H, d, *J* = 9.9 Hz, *Az* -4", 8"), 8.52 (1H, d, *J* = 7.5, 1.8 Hz, H-8), 9.1-9.2 (1H, m, H-6). ^{13}C-NMR (100 MHz, $CDCl_3$) δ:118.7, 119.2, 119.4, 119.9, 123.4, 123.6, 123.7, 123.9, 124.8, 125.3, 136.3, 137.7, 138.1, 138.3, 138.4, 138.6, 138.7, 138.9, 140.1, 140.2, 146.6, 147.2, 150.0, 152.4, 153.6, 153.7, 154.4. MS: *m/z* (rel. int. %) 383 (M^+, 79), 382 (100), 153 (16), 127 (8). IR (KBr): 3052, 3012, 1571, 822 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 248 (4.58), 283 (4.91), 313 (4.71), 388 (4.47), 604 (2.94), 641 (2.93), 699 (2.60). Anal. Calcd for $C_{27}H_{17}N_3$: C, 84.57; H, 4,47; N, 10.9. Found: C, 84.31; H, 4.74; N. 10.64.

2,3-Di(2-azulenyl)-6-azaquinoxaline (6c). A solution of **1** (50 mg, 0.16 mmol) and 3,4-diaminopyridine (**5c**) (22 mg, 0.20 mmol) in dry EtOH (20 mL) was refluxed for 26 h. The reaction mixture was treated by a method similar to that used for **6b** described above to give **6c** (54 mg, 87%) as dark blue needles (mp 204-205 °C, from EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.14 (4H, t, *J* = 9.8 Hz, *Az* -5', 7', 5", 7"), 7.5-7.6 (6H, m, *Az* -1', 3', 6', 1", 3", 6"), 8.01 (1H, d, *J* = 5.8 Hz, H-8), 8.25 (4H, d, *J* = 9.8 Hz, *Az* -4', 8', 4", 8"), 8.80 (1H, d, *J* = 5.8 Hz, H-7), 9.62 (1H, s, H-5). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 119.0, 119.2, 121.4, 123.8, 123.9, 136.4, 138.5, 138.6, 138.9, 139.0, 140.2, 143.7, 146.7, 146.8, 147.1, 153.0, 154.5, 155.5. MS: *m/z* (rel. int. %) 383 (M^+, 77), 382 (100), 153 (14), 127 (9). IR (KBr): 3052, 3012, 1574, 822 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 223 (4.51), 249 (4.57), 291 (4.91), 386 (4.41), 606 (2.94), 640 (2.93), 702^{sh} (2.60). Anal. Calcd for $C_{27}H_{17}N_3$: C, 84.57; H, 4.47; N, 10.96. Found: C, 84.98; H, 4.60; N, 10.82.

6,7-Diamino-2,3-(2-azulenyl)quinoxaline (6d). A solution of **1** (100 mg, 1.74 mmol), 1,2,4,5-benzenetetramine tetrahydrochloride (**5d**) (83 mg, 0.29 mmol) and pyridine (0.14 mL, 1.74 mmol) in dry EtOH (40 mL) was refluxed for 1 h. The reaction mixture was diluted with water and extracted with $CHCl_3$. The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a residue. The residue was chromatographied on silica gel with AcOEt to give **6d** (125 mg, 94%) as brown crystals (mp 190-193 °C, from EtOH). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 3.99 (4H, brs, $-NH_2$), 7.08 (4H, t, *J* = 9.8 Hz, *Az* - 5', 7', 5", 7"), 7.35 (2H, s, H-5, 8), 7.50 (2H, t, *J* = 9.8 Hz, *Az* -6', 6"), 7.52 (4H, s, *Az* -1', 3', 1", 3"), 8.18 (4H, d, *J* = 9.8 Hz, *Az* -4', 8', 4", 8"). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 110.5, 110.8, 118.7, 119.1, 123.1, 123.4, 137.1, 137.5, 138.8, 140.2, 147.6, 149.1. MS: *m/z* (rel. int. %) 412 (M^+, 72), 411 (100), 334 (12), 205 (12). IR (KBr): 3345, 3045, 3004, 1571, 1500, 1230, 825 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 233 (4.56), 273 (4.70), 295 (4.77), 312^{sh} (4.71), 430 (4.55), 580 (3.06), 625 (2.97), 692 (2.68). Anal. Calcd for $C_{28}H_{20}N_4$: C, 81.53; H, 4.89; N, 12.58. Found: C, 81.09; H, 4.77; N, 12.38.

2,3-Di(2-azulenyl)dibenzo[*f,h*]quinoxaline (6e). A solution of **1** (30 mg, 0.10 mmol) and 9,10-diaminophenanthlene (**5e**) (22.0 mg, 0.11 mmol) in dry EtOH (15 mL) was refluxed for 21 h. The reaction mixture was diluted with water and extracted with $CHCl_3$. The organic layer was dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a residue. The residue was chromatographied on silica gel with AcOEt-hexane (1:1) to give **6e** (25 mg, 75%) as yellowish green plates (mp 275-277 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.13 (4H, t, J = 9.8 Hz, *Az* -5', 7', 5", 7"), 7.55 (2H, t, J = 9.8 Hz, *Az* -6', 6"), 7.79 (4H, s, *Az* -1', 3', 1", 3"), 7.7-7.8 (4H, m, H-6, 7, 10, 11), 8.27 (4H, d, J = 9.8 Hz, *Az* -4', 8', 4", 8"), 8.65 (2H, d, J = 7.8 Hz, H-8, 9), 9.41 (2H, d, J = 8.3 Hz, H-5, 12). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 119.1, 122.8, 123.5, 125.8, 127.6, 129.3, 130.1, 131.7, 137.7, 137.8, 138.9, 140.4, 148.4, 148.9. MS: *m/z* (rel. int. %) 482 (M^+, 87), 481 (100), 240 (21), 177 (3), 127 (2). IR (KBr): 3131, 3095, 3045, 3012, 1571, 825 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 238 (4.69), 259 (4.71), 282 (4.90), 329 (4.71), 409 (4.57), 597 (2.90), 638 (2.87), 702 (2.53), Anal. Calcd for $C_{36}H_{22}N_2$: C, 89.60; H, 4.60; N, 5.81. Found: C, 89.41; H, 4.60; N, 5.79.

2,2',3,3'-Tetra(2-azulenyl)-6,6'-biquinoxaline (6f). A solution of **1** (80 mg, 0.26 mmol) and 3,3'-diaminobenzidine (**5f**) (30 mg, 0.14 mmol) in dry EtOH (30 mL) was refluxed for 45 h. The reaction mixture was treated by a method similar to that used for **6e** described above to give **6f** (52 mg, 54%) as yellowish green powder (mp > 300 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.13 (8H, t, J = 9.8 Hz, *Az*-5", 7", 5"', 7"', 5"", 7"", 5""', 7"""), 7.56 (4H, t, J = 9.8 Hz, *Az* - 6", 6"', 6"", 6"""), 7.62 (8H, s, *Az* -1", 3", 1"', 3"', 1"", 3"", 1""', 3"""), 8.26 (8H, d, J = 9.8 Hz, *Az* -4", 8", 4"', 8"', 4"", 8"", 4""', 8"""), 8.35 (4H d, J = 8.5 Hz, H-7, 8, 7', 8'), 8.65 (2H, s, H-5, 5'). IR (KBr): 3091, 3012, 2991, 2970, 2924, 2850, 1571, 839 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 250 (4.80), 298 (5.11), 418 (4.85), 599 (3.24), 638 (3.21), 708 (2.85). Anal. Calcd for $C_{56}H_{34}N_4$: C, 88.16; H, 4.49; N, 7.34. Found: C, 88.42; H, 4.68; N, 7.06.

2,3-Di(2-azulenyl)-6-benzoylquinoxaline (6g). A solution of **1** (50 mg, 0.16 mmol) and 3,4-diaminobenzophenone (**5g**) (39 mg, 0.18 mmol) in dry EtOH (20 mL) was refluxed for 51 h. The reaction mixture was treated by a method similar to that used for **6e** described above to give **6g** (73 mg, 93%) as yellowish green crystals (mp 221-222 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.11 (4H, t, J = 9.8 Hz, *Az* -5', 7', 5", 7"), 7.5-7.7 (5H, m, *Az* - 6', 6", *Ph* -3, 4, 5), 7.56 (2H, s, *Az* - 1', 3'), 7.59 (2H, s, *Az* -1", 3"), 7.92 (2H, d, J = 7.8 Hz, *Ph* -2, 6), 8.22 (2H, d, J = 9.8 Hz, *Az* -4', 8'), 8.23 (2H, d, J = 9.8 Hz, *Az* -4", 8"), 8.2-8.3 (2H, m, H-7, 8), 8.55 (2H, d, J =1.5 Hz, H-5). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 118.7, 118.9, 119.1, 119.3, 123.6, 123.9, 128.3, 128.7, 129.5, 129.9, 130.0, 130.3, 132.4, 132.9, 139.3, 138.2, 138.5, 138.7, 140.2, 143.1, 147.2, 147.3, 152.2, 152.7, 195.9. MS: *m/z* (rel. int. %) 486 (M^+, 94), 485 (100), 381 (12), 127 (5), 108 (28), 77 (40). IR (KBr): 3055, 1654, 1572, 1167, 829 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log

ε): 249 (4.62), 296 (4.96), 298^{sh} (4.95), 602 (2.93), 638 (2.91), 705^{sh} (2.57). Anal. Calcd for $C_{35}H_{22}N_2O$: C, 86.40; H, 4.56; N, 5.76. Found: C, 86.64; H, 4.78; N, 5.83.

Diazuleno[2,1-*a*:1,2-*c*]phenazine (8) A solution of **6a** (50 mg, 0.13 mmol) and activated manganese dioxide (230 mg, 2.65 mmol) in benzene (15 mL) was refluxed for 27 h. The reaction mixture was purified by column chromatography on silica gel with CH_2Cl_2 to afford the recovered **6a** (27 mg, 54%) and **8** (10 mg, 20%) as yellowish brown crystals (mp 270-271 °C). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.2-7.3 (4H, m, H-2, 4, 7, 9), 7.69 (2H, t, J =9.9 Hz, H-3, 8), 7.88 (2H, m, H-14, 15), 8.40 (2H, m, H-13, 16), 8.54 (2H, d, J =10.1 Hz, H-1, 10), 8.64 (2H, s, H-11, 18), 9.35 (2H, d, J =9.2 Hz, H-5, 6). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 116.2, 123.0, 123.7, 124.1, 129.5, 129.9, 135.5, 136.7, 139.5, 139.6, 140.0, 142.3, 143.3. MS: *m/z* (rel. int. %) 380 (M^+, 100), 328 (1), 276 (1), 190 (13), 126 (1). IR (KBr): 3047, 1568, 1136, 760 cm^{-1}. UV-VIS (CH_2Cl_2) λ_{max} (log ε): 265 (4.59), 312 (4.79), 330^{sh} (4.72), 368^{sh} (4.56), 407 (4.49), 435^{sh} (4.33), 462 (4.24), 636^{sh} (2.79), 719 (3.03), 777 (3.03). Anal. Calcd for $C_{28}H_{16}N_2$: C, 88.14; H, 4.24; N, 7.36. Found: C, 88.14, H, 4.11, N, 7.06.

X-ray structural analysis of 6a. Reflection data were collected on a Rigaku Mercury CCD diffractometer with Mo-Kα radiation (λ = 0.71070 Å) at 295 K. All the structures were solved by the direct method and refined by full-matrix least-squares method on F^2 with SHELX-97.[5] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model. Crystal data are as follows: $C_{28}H_{18}N_2$, M = 382.44, monoclinic, space group $P2_1/c$, a = 6.1404(18), b = 24.158(7), c = 13.302(4) Å, β = 91.849(1)°, V = 1972.2(10) Å^3, Z = 4, D_c = 1.288 g cm^{-1}, F(000) = 800, μ(Mo-Kα) = 0.76 cm^{-1}, crystal dimensions = 0.40 × 0.075 × 0.05 mm, 15659 reflections collected, 4501 independent (R_{int} = 0.0492), R_1 = 0.0748 and wR_2 = 0.2504 for 3200 data with $I > 2\sigma(I)$. CCDC 695852 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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