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Synthesis, Molecular Structure, and Properties of 2-(2-Hydroxyphenyl)-1azaazulene

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We herein report the synthesis of 2-(2-methoxyphenyl)-1azaazulene ($\mathbf{8}$) by a Suzuki–Miyaura cross-coupling reaction between 2-chloro-1-azaazulene and 2-methoxyphenylboronic acid and also by the condensation of tropone and the ylide derived from 1-(*o*-methoxyphenacyl)pyridinium iodide. Demethylation of $\mathbf{8}$ afforded the title compound $\mathbf{6}$. X-ray crystallographic analysis of $\mathbf{6}$ provided evidence for an intramolecular hydrogen bond between the phenolic hydrogen atom and the nitrogen atom of the azaazulenyl ring and also revealed its coplanar ring system. We also report the acidity, basicity, and absorption and emission behavior of $\mathbf{6}$.

Introduction

Azaazulenes, heteroatomic analogues of azulene, have long been attractive to organic chemists for their basic physical and chemical properties and potential biological activity.^[1] Among the various azaazulenes, 1-azaazulenes have been most studied because of their stability and facile accessibility. In addition to the classical synthetic methods involving condensation reactions of troponoid substrates with carbon fragments corresponding to the five-membered ring of 1-azaazulene explored by Nozoe^[2] and Nitta^[3] and their co-workers, Narasaka and co-workers have recently developed a novel synthesis of 1-azaazulenes by a palladiumcatalyzed amino-Heck reaction,^[4] and Deprés and coworkers have reported that cycloheptatriene/dichloroketene adducts can be converted into 1-azaazulenes.^[5] In addition to the development of these synthetic methods, recent transition-metal-catalyzed cross-coupling and amination reactions have facilitated the derivatization of halogen-substituted 1-azaazulenes to afford various functionalized 1-azaazulenes.^[6,7] Meanwhile, interest in substituted 1-azaazulenes as ligands has recently increased. In 1998, Sugihara et al. reported for the first time on the use of 8-(methylamino)-3-phenyl-1-azaazulene (1)^[8] as a bidentate ligand. Later, we and Abe et al. reported the interactions of other 1-azaazulenes, $2^{[9]}, 3^{[10]}, 4^{[11]}$ and $5^{[11]}$ with metal ions. All these ligands have only amino and imino nitrogen atoms. To in-

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vestigate the efficiency of the combination of an imino nitrogen atom and a phenolic oxygen atom in a 1-azaazulenyl ligand, we became interested in the title compound, 2-(2hydroxyphenyl)-1-azaazulene (**6**), the structure of which is related to 8-hydroxyquinoline (**7**),^[12] one of the most widely used chelating reagents. In this paper we describe the synthesis, molecular structure, and physical properties (for example, absorption and emission behavior, acidity and basicity) of 1-azaazulene **6** (Scheme 1).



Scheme 1. Title molecule 6 and structurally related compounds.

Results and Discussion

Compound 6 was synthesized by two methods via its methoxy derivative 8, as shown in Scheme 2. Compound 8

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was synthesized either by condensation^[13] of tropone (9) with pyridinium salt 10 in the presence of ammonium acetate or by Suzuki-Miyaura cross-coupling^[14] between 2chloro-1-azaazulene $(11)^{[2]}$ and (2-methoxyphenyl)boronic acid (12). Note that [(A-^{ta}Phos)₂PdCl₂]^[15] (Scheme 3) served as an efficient palladium catalyst in the latter coupling reaction with 11, because it is known that 11 is notoriously less active in the Suzuki-Miyaura coupling reactions than 2-bromo- and 2-iodo-1-azaazulenes.^[10] The title compound 6 was obtained in 78% yield by demethylation of 8 in hydrobromic acid at reflux. In the ¹H NMR spectrum of 6 in CDCl₃, the hydrogen atom of the hydroxy group appears as a broad signal at $\delta = 14.22$ ppm, which suggests that it forms a hydrogen bond with the nitrogen atom of the azaazulene ring. Other resonances appear in the aromatic region, and their vicinal coupling constants suggest that there is no C-C bond alternation in either the phenol ring or the seven-membered ring of the azaazulenyl moiety. The signals in the ¹H and ¹³C NMR spectra were assigned on the basis of 2D NMR spectra and NOE experiments, as shown in Figure 1.



Scheme 2. Synthesis of 6.



Scheme 3. Structure of [(A-taPhos)₂PdCl₂].

Furthermore, the detailed structure of **6** was determined by X-ray crystallographic analysis. Figure 2 shows ORTEP drawings of **6**, revealing its coplanar structure. Bond lengths show the convergence of C–C bonds in the seven-membered and phenolic rings, which is consistent with the structure determined on the basis of the NMR coupling constants. The distance between the oxygen atom and the nitrogen atom is 2.583 Å, fingerprinting the intramolecular hydrogen bond.



Figure 2. X-ray structure of **6**. Bond lengths [Å]: N1–C2 1.365(3), C2–C3 1.401(3), C3–C3a 1.390(3), C3a–C4 1.388(3), C4–C5 1.378(3), C5–C6 1.394(4), C6–C7 1.382(4), C7–C8 1.386(3), C8–C8a 1.388(4), C3a–C8a 1.470(3), C8a–N1 1.353(3), C2–C1' 1.456(3), C1'–C2' 1.403(3), C2'–C3' 1.376(3), C3'–C4' 1.385(4), C4'–C5' 1.367(4), C5'–C6' 1.392(3), C6'–C1' 1.408(3), C2'–O7' 1.353(3).

The UV/Vis spectra of 3, 6, and 2-phenyl-1-azaazulene (13: Scheme 4)^{$[1\bar{3}]$} in acetonitrile are shown in Figure 3. Four absorption bands were observed for these 1-azaazulenes, and the long-wavelength absorption of 6 displays a slight blueshift with a substantial hyperchromic effect compared with those of 3 and 13. This blueshift and hyperchromic effect can be attributed to the intramolecular protonation resulting from the presence of the hydrogen bond. The long-wavelength absorption maximum of 6 appears to depend on the polarity of the solvent. The maximum shows a redshift in more polar solvents (Figure 4; left). The difference between the dependence on protic and aprotic solvents is not clearly observed for 6. This is in contrast to the case of 3. Although a similar redshift is observed for 3, the shift is different in the two series of protic and aprotic solvents (Figure 4; right). The phenomenon seen for 6 must be due to the restricted conformational change around the C-C single bond between the 1-azaazulenyl and phenol rings,



Figure 1. ¹H and ¹³C NMR signal assignment (left) and NOE experiment (right) for 6.

that is, **6** exists mainly as the conformer with the intramolecular hydrogen bond. Therefore, the conformation of **6** is limited and less affected by solvent polarity. On the other hand, **3** exists as conformer **A** in aprotic solvents, which is the most stable structure based on DFT calculations,^[16] whereas **3** exists in protic solvents as conformer **B** forming two intermolecular hydrogen bonds with the solvent (Scheme 5). This conformational change around the C–C single bond between the 1-azaazulenyl and pyridyl rings in **3** leads to the difference in the two series of protic and aprotic solvents.

Scheme 4. Structures of 13 and 14.

Figure 3. UV/Vis spectra of **3**, **6**, and **13** in acetonitrile in the region of 200–600 nm (top) and the expanded region of 400–600 nm (bottom).

The UV/Vis spectrum of **6** varies with pH, as shown in Figure 5. The long-wavelength maximum shows a clear blueshift in acidic solution and a redshift in basic solution. Based on these changes, the acidity (pK_a) and basicity (pK_b)

Figure 4. Dependence of the long-wavelength absorption maxima of **3** (right) and **6** (left) on the dielectric constants of solvents. Symbols for solvents are as follows: Ethylene glycol (\bigcirc), methanol (\bigcirc), ethanol (\triangle), 1-butanol (\triangle), acetonitrile (\blacksquare), acetone (\square), ethyl acetate (\blacklozenge), and dioxane (\diamondsuit).

Scheme 5. Two major conformers, A and B, for 3 and the doubly hydrogen-bonded structure of conformer B.

of **6** were determined by the titration method.^[17] Because the solubility of **6** in water is very poor, measurements were carried out in 50% aqueous EtOH. The values, including those of structurally related compounds such as phenol,^[18] pyridine,^[18,19] **3**, **7**,^[20,21] **13**, and 2-(2-hydroxyphenyl)pyr-

Figure 5. UV/Vis spectra of 6 in acidic, neutral, and basic solutions.

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idine (14),^[22] are shown in Table 1. Although different solvent systems were used to measure the acidity and basicity of these compounds, the following conclusions were drawn from these data. Compound **6** is a weaker acid than phenol, **7**, and **14**. Because the nitrogen atom at the 1-position of 1-azaazulene is more electronegative than the nitrogen atom of pyridine, the phenolate anion of **6** must be more destabilized. Compound **14** is a weaker base than pyridine, and it can be seen that **6** shows a similar tendency to 1-azaazul-

Compound	Acidity	Basicity	
	pK _a	pK_{b1}	pK_{b2}
3		7.98 ^[a]	11.58 ^[a]
6	12.7 ^[b]	8.7 ^[b]	
Phenol	11.3 ^[b]		
	9.99 ^[c]		
7	11.30 ^[d]	9.67 ^[d]	
	11.54 ^[e]	10.03 ^[e]	
13		7.18 ^[a]	
14	$10.2^{[f]}$	9.9 ^[f]	
Pyridine		8.99 ^[c]	
,		8.9 ^[g]	
		8.7 ^[h]	

Table 1. Acidity and basicity of 6 and related compounds.

[a] Measured in 50% aqueous CH₃CN; taken from ref.^[10] [b] Measured in 50% aqueous EtOH; this work. [c] Measured in water; taken from ref.^[17] [d] Measured in 75% aqueous EtOH; taken from ref.^[20] [e] Measured in 50% aqueous dioxane; taken from ref.^[21] [f] Measured in water; taken from ref.^[18] [h] Measured in 80% aqueous EtOH; taken from ref.^[19]

Figure 6. UV/Vis spectra of 6 in the presence of metal ions in acetonitrile (top) and the expanded spectra of the area in the rectangle (bottom).

enes 3 and 13. It is clear that the 2-hydroxyphenyl group in 6 and 14 masks the basicity of imines rather than increasing it by the electron-donating resonance effect.

Spectral changes were also observed for **6** in the presence of 100 equiv. of metal ions (Figure 6). Among the metal ions examined, Al³⁺, Sc³⁺, Pb²⁺, and Hg²⁺ led to a pronounced blueshift and hyperchromic effect. Compound **6** exhibits emissions at 444 and 561 nm upon excitation at 390 and 495 nm, respectively (Figure 7). The emission quantum yield of **6** was determined to be $\Phi = 1.4 \times 10^{-5}$ by comparison with that of anthracene.^[23] However, its emission quantum yield was found to be markedly higher in the presence of metal ions (Table 2). The quantum yields of **6** in the presence of Pb²⁺, Al³⁺, and Sc³⁺ ions are 10³ times higher than the quantum yield determined in the absence of ions, which suggests the potential for sensing these metal ions by **6**.

Figure 7. UV/Vis and emission spectra of 6.

Table 2. Photophysical data of $\mathbf{6}$ in the presence of metal ions in acetonitrile.

Metal cation ^[a]	λ_{\max}^{abs} [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]	λ_{\max}^{em} [nm]	Φ
Na ⁺	390	11501	445	8.0×10^{-4}
Ag^+	390	11339	444	4.4×10^{-4}
Mg^{2+}	462	9034	526	5.0×10^{-3}
Ca ²⁺	477	5291	525	5.7×10^{-3}
Zn^{2+}	459	13132	527	9.7×10^{-3}
Ni ²⁺	461	7995	526	1.4×10^{-3}
Hg^{2+}	456	14853	526	1.2×10^{-3}
Pb^{2+}	456	14881	526	1.2×10^{-2}
Cd^{2+}	468	7406	528	1.3×10^{-3}
Sc ³⁺	457	14512	528	1.3×10^{-2}
A1 ³⁺	456	14945	526	1.1×10^{-2}

[a] Perchlorate salts were used except for the scandium ion for which the triflate salt was used.

Conclusions

It has been demonstrated that the novel 1-azaazulene derivative $\mathbf{6}$ with a phenol functional group at the 2-position can be synthesized by two simple methods via its methoxy derivative $\mathbf{8}$. The structure of $\mathbf{6}$ was confirmed by spectroscopic and X-ray crystallographic analyses, the presence of its aromatic and coplanar nature as well as an intramolecular hydrogen bond being supported by a relatively intense absorption in the visible light range and by the X-ray diffraction data. The long-wavelength absorption band of 6shifts in the presence of several metal ions and, its emission upon excitation was clearly enhanced.

Experimental Section

General: Melting points were measured with a Yanaco M-3 instrument. IR spectra were recorded with a JEOL Diamond-20 spectrometer. UV/Vis spectra were recorded with a Shimadzu UV-2550 spectrometer. Emission spectra were recorded with a Shimadzu RT-5300PC spectrometer. ¹H and ¹³C NMR spectra were recorded with a JEOL $\lambda 400$ spectrometer by using tetramethylsilane as internal standard. Mass spectra were recorded with a JMS-700 mass spectrometer. Column chromatography was performed with Merck neutral alumina-90. 2-Methoxyacetophenone was purchased from Tokyo Chemical Industry, Inc. (2-Methoxyphenyl)boronic acid and [(A-taPhos)₂PdCl₂] were purchased from Aldrich Chem. Co. Tropone was prepared by selenium oxide oxidation of cycloheptatriene.^[24] Compound 3 was prepared from tropone according to our previously reported method.^[10] Compound 11 was prepared from 2-aminotropone according to the method of Nozoe and coworkers.^[2] Compound 13 was prepared from tropone according to the method of Sugimura et al.^[13]

1-(2-Methoxyphenacyl)pyridinium Iodide (10): A solution of 2methoxyacetophenone (2.01 g, 13.4 mmol) and iodine (3.39 g, 13.3 mmol) in pyridine (50 mL) was heated at reflux under nitrogen for 22 h. Solids formed were removed by filtration, and the filtrate was concentrated. The residue was crystallized from dichloromethane to give 3.71 g (80% yield) of 10 as buff microcrystals. M.p. 159–160 °C. ¹H NMR (CDCl₃): δ = 4.07 (s, 3 H), 6.57 (s, 2 H), 7.02 (t, J = 7.9 Hz, 1 H), 7.05 (d, J = 7.9 Hz, 1 H), 7.60 (t, J =7.9 Hz, 1 H), 7.88 (d, J = 7.9 Hz, 1 H), 8.10 (m, 2 H), 8.61 (t, J = 7.8 Hz, 1 H), 9.15 (d, J = 5.8 Hz, 2 H) ppm. ¹³C NMR (CDCl₃): $\delta = 56.9, \, 70.8, \, 112.4, \, 121.0, \, 122.6, \, 127.7, \, 131.1, \, 136.7, \, 146.0, \, 146.2,$ 160.5, 189.0 ppm. IR (KBr): $\tilde{v}_{max} = 3465$ (m), 3388 (m), 3093 (w), 3049 (w), 3030 (w), 1672 (s), 1635 (m), 1599 (s), 1489 (s), 1483 (s), 1468 (s), 1454 (w), 1439 (m), 1344 (m), 1286 (s), 1242 (s), 1209 (s), 1194 (m), 1178 (m), 1157 (s), 1117 (w), 1020 (s), 991 (m), 783 (w), 775 (s), 752 (m), 678 (m) cm⁻¹. MS (70 eV): m/z (%) = 228 (1) [C14H14NO2]⁺, 227 (2), 135 (100), 127 (10), 105 (10), 91 (30), 77 (21), 71 (38), 63 (15), 51 (26). C₁₄H₁₄INO₂ (355.2): calcd. C 47.34, H 3.97, N 3.94; found C 47.29, H 4.21, N 3.95.

2-(2-Methoxyphenyl)-1-azaazulene (8) from Tropone: A solution of 10 (3.58 g, 10.1 mmol), tropone (530 mg, 5.00 mmol), and ammonium acetate (5.40 g, 70.0 mmol) in acetic acid (20 mL) was heated at reflux under nitrogen for 12 h. The solvent was evaporated, and the residue was poured into an aqueous solution of NaHCO₃ and extracted with ethyl acetate (5 \times 50 mL). The combined organic layers were washed with a thiosulfate solution and brine. After drying with Na₂SO₄, the solvent was removed under reduced pressure, and the residue was purified by chromatography (Al₂O₃; 20% ethyl acetate/hexane) to give 681 mg (58% yield) of 8 as red prisms. M.p. 135–136 °C. ¹H NMR (CDCl₃): δ = 4.01 (s, 3 H), 7.05 (dd, J = 8.4, 1.0 Hz, 1 H), 7.15 (t, J = 7.4, 1.0 Hz, 1 H), 7.42 (ddd, J = 8.4, 7.4, 1.6 Hz, 1 H), 7.56 (t, J = 10.1 Hz, 1 H), 7.70 (t, J = 10.1 Hz, 1 H), 7.74 (t, *J* = 10.1 Hz, 1 H), 8.07 (s, 1 H), 8.50 (d, *J* = 10.1 Hz, 1 H), 8.63 (dd, J = 7.4, 1.6 Hz, 1 H), 8.65 (d, J = 10.1 Hz, 1 H) ppm. ¹³C NMR (CDCl₃): δ = 55.5, 111.4, 115.6, 121.1, 124.1, 128.4, 129.3, 130.9, 131.3, 134.6, 134.9, 136.2, 147.8, 157.4, 158.6, 164.2 ppm. IR (KBr): $\tilde{v}_{max} = 3513$ (w), 3477 (w), 3456 (w), 3440 (w), 3348 (w), 1599 (m), 1579 (w), 1498 (m), 1487 (m), 1464 (s),

1452 (s), 1433 (s), 1404 (s), 1282 (m), 1254 (s), 1240 (w), 1159 (w), 1065 (m), 1020 (s), 820 (m), 760 (s), 752 (s), 742 (s) cm⁻¹. UV (acetonitrile): λ_{max} [log ε] = 211 [4.35], 234 [3.95] 283 [4.43], 369 [3.96], 383 [3.99], 491 [3.27], 507 [3.27], 550 (sh) [2.92 M⁻¹ cm⁻¹] nm. MS (70 eV): *m/z* (%) = 235 (62) [M]⁺, 234 (100), 206 (54), 205 (58), 204 (53), 190 (15), 178 (18), 130 (22), 102 (26), 89 (15), 63 (17). C₁₆H₁₃NO·0.2H₂O (238.9): calcd. C 80.45, H 5.65, N 5.86; found C 80.37, H 5.52, N 5.97.

2-(2-Methoxyphenyl)-1-azaazulene (8) from 2-Chloro-1-azaazulene: A reaction vessel with a mixture of **11** (100 mg, 0.61 mmol), **12** (111 mg, 0.73 mmol), $[(A^{-ta}Phos)_2PdCl_2]$ (13 mg, 18.4 µmol), and Cs_2CO_3 (397 mg, 1.22 mmol) in DMF/H₂O (10:1; 3.5 mL) was evacuated and flushed with argon (5×). This mixture was heated in an oil bath at 140 °C under argon by using a balloon for 12 h. The resulting reaction mixture was poured into a 10% EDTA/NaHCO₃ solution (30 mL) and extracted three times with toluene (20 mL). The combined organic layers were washed with a 1 N NaOH aqueous solution and brine, and dried with MgSO₄. The solvent was removed, and the residue was purified by chromatography to give 97 mg of **8** (67% yield).

2-(2-Hydroxyphenyl)-1-azaazulene (6): A solution of 8 (470 mg, 2.00 mmol) in 48% HBr (40 mL) was heated at reflux for 12 h. The resulting reaction mixture was carefully poured into an aqueous solution of NaHCO₃ and extracted with dichloromethane (5× 20 mL). The combined organic layers were washed with brine. After drying with Na₂SO₄, the solvent was removed under reduced pressure, and the residue was purified by chromatography (Al₂O₃; 20% ethyl acetate/hexane) to give 344 mg (78% yield) of 6 as vermilion prisms. M.p. 160–162 °C. ¹H NMR (CDCl₃): δ = 6.96 (td, J = 7.8, 1.2 Hz, 1 H), 7.10 (dd, J = 8.4, 1.2 Hz, 1 H), 7.35 (ddd, J = 8.4, 7.8, 1.2 Hz, 1 H), 7.63 (t, J = 9.4 Hz, 1 H), 7.70 (s, 1 H), 7.73 (t, J = 9.4 Hz, 1 H), 7.78 (t, J = 9.4 Hz, 1 H), 7.96 (dd, J = 7.8, 1.2 Hz, 1 H), 8.49 (d, J = 9.4 Hz, 1 H), 8.55 (d, J = 9.4 Hz, 1 H), 14.22 (br. s, 1 H) ppm. IR (KBr): $\tilde{v}_{max} = 3446$ (w), 1616 (m), 1589 (m), 1571 (w), 1541 (w), 1508 (m), 1473 (s), 1441 (m), 1412 (s), 1304 (m), 1290 (w), 1275 (w), 1261 (s), 1216 (m), 1117 (w), 1041 (w), 1034 (w), 939 (w), 885 (w), 874 (w), 858 (w), 831 (s), 800 (s), 754 (s), 748 (s), 739 (s), 725 (m) cm⁻¹. UV (acetonitrile): $\lambda_{max} [\log \varepsilon]$ = 211 [4.42], 237 [4.10], 281 [4.55], 311 [4.23], 375 [3.90], 390 [3.97], 479 [3.60], 495 [3.61], 532 (sh) [3.29 m⁻¹ cm⁻¹] nm. MS (70 eV): *m*/*z* $(\%) = 222 (17) [M + 1]^+, 221 (100) [M]^+, 193 (41), 192 (19), 191$ (14), 167 (11), 97 (11), 84 (13). $C_{15}H_{11}NO \cdot 0.2H_2O$ (224.9): calcd. C 80.12, H 5.11, N 6.23; found C 80.09, H 4.96, N 6.42. The 6 HBr salt was obtained in quantitative yield as orange microcrystals by reaction of 6 with 48% HBr in ethanol. M.p. >230 °C (dec.). ¹H NMR (CDCl₃): δ = 7.12 (t, J = 7.7 Hz, 1 H), 7.22 (d, J = 7.7 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 1 H), 8.15 (d, J = 7.7 Hz, 1 H), 8.28 (s, 1 H), 8.39 (t, J = 9.8 Hz, 1 H), 8.47 (t, J = 9.8 Hz, 1 H), 8.56 (t, J = 9.8 Hz, 1 H), 9.21 (d, J = 9.8 Hz, 1 H), 9.23 (d, J = 9.8 Hz, 1 H), 11.35 (s, 1 H), 14.43 (s, 1 H) ppm. ¹³C NMR (CDCl₃): δ = 112.6, 114.4, 117.2, 120.2, 130.0, 133.3, 134.0, 136.6, 136.8, 141.7, 143.9, 144.8, 147.3, 157.4, 166.0 ppm. IR (KBr): $\tilde{v}_{max} = 3437$ (s), 3078 (s), 1608 (s), 1589 (w), 1566 (m), 1537 (m), 1491 (m), 1460 (s), 1452 (s), 1439 (s), 1398 (w), 1379 (w), 1333 (m), 1279 (w), 1252 (w), 1238 (m), 1159 (m), 829 (m), 825 (m), 760 (s), 741 (m), 694 (w) cm⁻¹. UV (acetonitrile): $\lambda_{max} [\log \varepsilon] = 211$ [4.49], 238 [4.18], 282 [3.10], 375 (sh) [4.00], 390 [4.06], 473 [3.66], 496 [3.68], 532 (sh) $[3.36 \text{ M}^{-1} \text{ cm}^{-1}]$ nm. C₁₅H₁₂BrNO·1/3H₂O (308.2): calcd. C 58.47, H 4.41, N 4.55; found C 58.42, H 4.22, N 4.45.

Determination of the Acidity and Basicity of 6: The acidity and basicity of 6 were determined from the titration curves based on pH-dependent absorption spectra in 50% aqueous ethanol solu-

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tions by a curve-fitting method using the KaleidaGraph program.^[25] For acidity, the absorption peaks at 389, 445, and 495 nm were used, and for basicity, the absorption peak at 456 nm. Boronic acid buffer solutions were used in the range of pH = 2.09-8.53 and NaOH solutions in the range of pH = 11.1-13.9.

X-ray Crystallographic Analysis of 6: Diffraction measurements were carried out with a Rigaku AFC7R diffractometer. The crystal data are as follows: monoclinic, space group, $P2_1/c$ (#14), a = 11.168(3), b = 6.039(2), c = 16.659(2) Å, $\beta = 103.43(2)^\circ$, V = 1092.8(5) Å³, Z = 4, R = 0.057, wR = 0.114, and R1 = 0.046 [$I > 2.0\sigma(I)$]. CCDC-814552 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.

Supporting Information (see footnote on the first page of this article): Calculated energy profile for rotation of the C–C single bond of **3**, data for the determination of the acidity and basicity of **6**, and ¹H and ¹³C NMR spectra of the new compounds.

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