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SYNTHESIS, STRUCTURE AND SPECTROSCOPIC CHARACTERISTICS OF 2'-BORYL-4''-DIMETHYLAMINO-CHALCONES. EFFECT OF AN INTRAMOLECULAR BORON-OXYGEN COORDINATE BOND TO THE CONJUGATED SYSTEM

Toshihiro Murafuji,* Kenji Sugimoto, Sachiko Yanagimoto, Tomokazu Moriya, Yoshikazu Sugihara,* Yuji Mikata,† Masako Kato,†† and Shigenobu Yano†

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

†Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630-8506, Japan

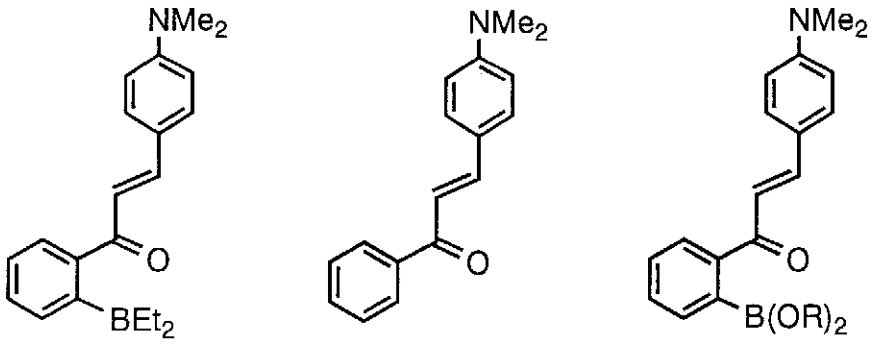
††Divison of Material Science, Graduate School of Human Culture, Nara Women's University, Nara 630-8506, Japan

Abstract – 2'-Diethylboryl-4''-dimethylaminochalcone (**1**) and the related compounds (**4**)–(**7**) bearing a dioxyboryl group in the 2'-position were synthesized, and the effect of the intramolecular boron–oxygen coordinate bond on the spectroscopic characteristics of 4''-dimethylaminochalcone chromophore was examined by comparison with 4''-dimethylaminochalcone (**2**) using UV/VIS and fluorescence spectra.

INTRODUCTION

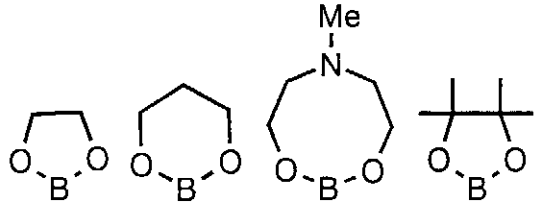
Construction of organometallics based on the coordinate bond between the metal center and the ligands is an area of research that has grown tremendously in recent years. It is an important issue for us to examine how coordination affects molecular structure and properties.[1] Recently, we have reported the structure and spectroscopic characteristics of 2'-diethylboryl-4''-dimethylaminochalcone (**1**) bearing an intramolecular boron–oxygen coordinate bond in comparison with 4''-dimethylaminochalcone (**2**).[2] It has been found that, when compared with the respective ground states, the polarity of the exited state of **2** is greater than that of **1** due to the more polarized ground state of **1**, which is brought about by the formation of the coordinate bond. In order to examine the effect of the coordinate bond to the properties

of the conjugated system furthermore, we decided to study a series of compounds (**4**)–(**7**) which possess a dioxyboryl group in place of the diethylboryl group at the 2'-position of **1**. The difference of the Lewis acidity between the boryl groups is considered to be reflected in the 4''-dimethylaminochalcone chromophore. In this paper, we describe the synthesis of **4–7** and their spectroscopic characteristics compared with those of **1** and **2**.



1

2



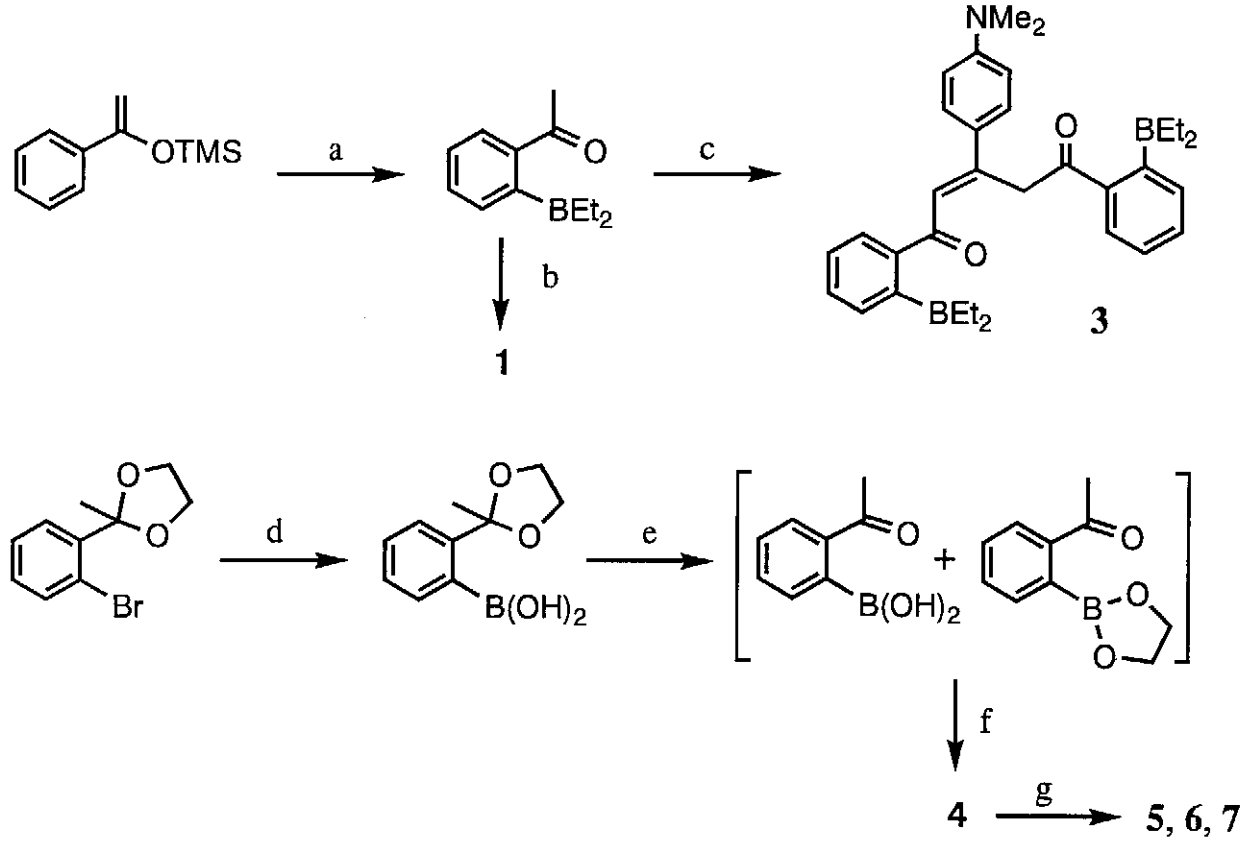
4 **5** **6** **7**

RESULTS AND DISCUSSION

The synthetic routes of the conjugated boron compounds are summarized in Scheme 1. These routes are based on the aldol condensation but are different from the simple synthesis of **2** from 4-dimethylaminobenzaldehyde (DMAB) and acetophenone with potassium hydroxide since the high affinity of a boron center toward oxy functional groups or bases sensitively affects the condensation reaction. We used, therefore, potassium *tert*-butoxide in place of potassium hydroxide. Attempted synthesis of **1** was, however, unsuccessful from 2'-diethylborylacetophenone and DMAB with potassium *tert*-butoxide in a mixture of benzene and *tert*-butyl alcohol and gave undesired **3**, which was considered to be formed *via* the Michael addition of the second enolate of 2'-diethylborylacetophenone to **1**. This result suggests that the electron density on the β-carbon of the enone part in **1** is lowered through the intramolecular boron–oxygen coordinate bond, which is consistent with the downfield shift of the β-carbon signal of **1** (δ 150.51) compared with that of **2** (δ 146.21) in the ^{13}C NMR spectra. Eventually, **1** could be synthesized by using LDA in ether without the formation of **3**. The difference between both reactions is attributed to the stabilization of an intermediate as lithium β-ketoalkoxide, which blocks the second Michael addition. Synthesis of **4** was started from the boronic acid. In the deacetalization of the carbonyl group with *p*-toluenesulfonic acid, fortunately, transacetalization to the boron atom occurred to give the five-membered boronic ester, which could omit the protection of the hydroxy groups on the boron atom in the subsequent

aldol condensation employing strongly basic conditions. When the cyclic boronic ester was allowed to react with DMAB in the presence of potassium *tert*-butoxide (3 equiv) in THF–*tert*-butyl alcohol (1:1), yellow solids separated out from the reaction mixture after work-up with brine. Decrease of the amount of potassium *tert*-butoxide employed lowered the amount of the solids. They are soluble in polar solvents such as MeOH, DMSO, acetone, pyridine and water. The aqueous solution shows alkaline and the flame reaction detects the presence of sodium ion. The ^{1}H NMR spectrum measured in pyridine-d_5 exhibits the presence of the 4''-dimethylaminochalcone skeleton and the non-equivalent proton signals of two methylene groups of the boryl group. Furthermore, one proton signal due to a hydroxy group (δ 3.3), which disappears by adding D_2O, is observed. No signals due to a *tert*-butyl group are observed. From these results, we tentatively propose the structure of sodium salt of boronic acid monoester, $ArB(ONa)OCH_2CH_2OH$ (Ar = 4''-dimethylaminochalcone skeleton). Interestingly, the IR spectrum shows carbonyl stretching vibration in a lowerd wavenumber region (1597 cm^{-1}) compared with

Scheme 1



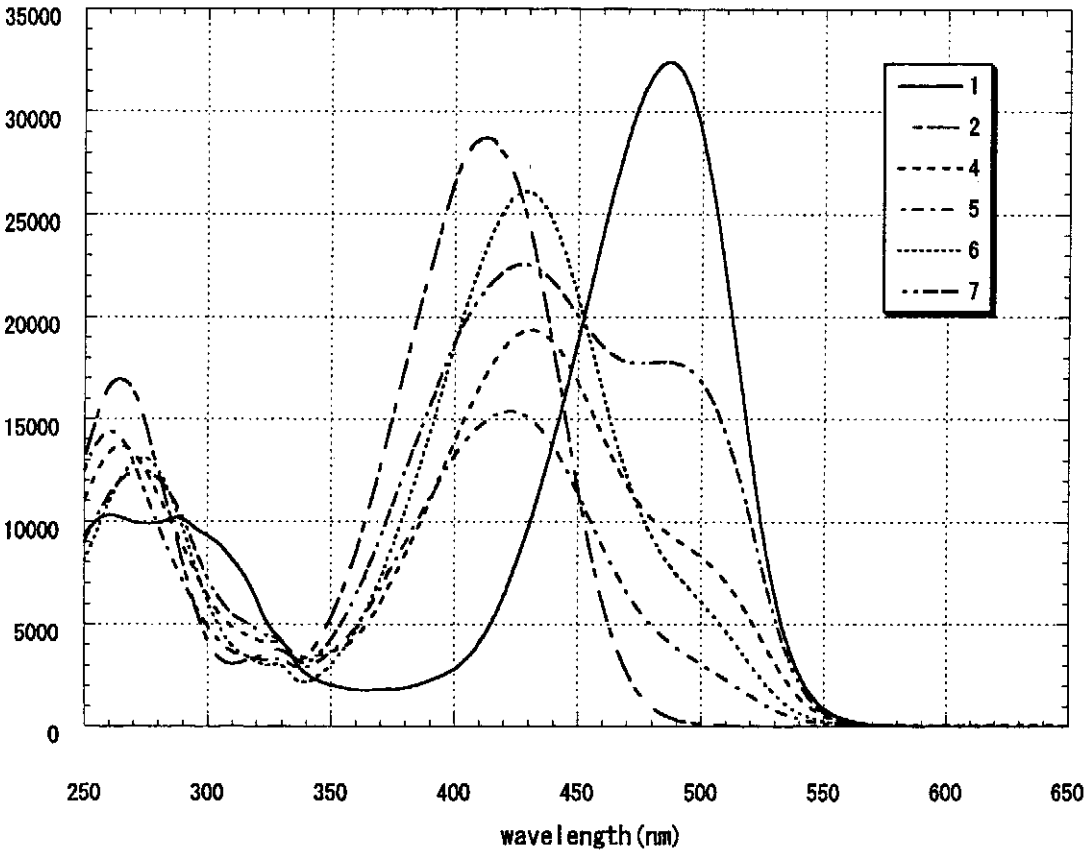
Reagents: (a) *n*-BuLi (3 equiv), TMEDA (3 equiv), hexane, rt; Et_2BOMe (2 equiv), rt; brine; (b) LDA (1.1 equiv), DMAB (1 equiv), Et_2O, rt; brine; (c) DMAB (1 equiv), *t*-BuOK (1.3 equiv), C_6H_6–*t*-BuOH (1:1 v/v), rt; (d) *n*-BuLi (1 equiv), $B(OPr\text{-}i)_3$ (1 equiv), THF, –78 °C to rt; brine; (e) TsOH (0.01 equiv), acetone, then removal of acetone; (f) DMAB (1 equiv), *t*-BuOK (3 equiv), THF–*t*-BuOH (1:1 v/v), 0 °C; brine, then conc. HCl–MeOH (1:1 v/v), neutralization with $NaHCO_3$; (g) diol (1.0 equiv), CH_2Cl_2, rt

2 (1650 cm^{-1}), which suggests the presence of the intramolecular coordinate bond between the boron and carbonyl oxygen atoms. Hydrolysis of this salt under acidic conditions followed by neutralization afforded **4**. Compound (**4**) underwent transacetalization with some diols (1 equiv) in dichloromethane at room temperature to give the corresponding cyclic boronic esters (**5**)–(**7**). These reactions proceeded almost completely and did not give a mixture containing the starting boronic esters, which is suggestive of the stability of **5**–**7** in preference to **4**. The main reason in the respective reactions may be the electronic factor at the boron center and/or the steric one around the boron atom, that is, the higher Lewis acidity of the boron center of **4** than that of **5**,[3] the rigid conformation and lowered Lewis acidity of the boron center in **6** by the tridentate ligand through an transannular boron–nitrogen coordinate bond,[4a] and the steric blocking around the boron center of **7** by the four methyl groups which suppress the reverse reaction. Although a large excess (10 equiv) of ethanediol or *N*-methyldiethanolamine was allowed to react with **7**, each reaction proceeded scarcely.

While **1**, **4**, **5** and **7** are reddish-violet crystals, **6** is yellow crystals similar to **2**, indicating the absence of the intramolecular boron–oxygen coordinate bond. The measurement of ^{11}B NMR spectra revealed the respective chemical shifts (δ) of the boron atoms in **1**(14.8), **4** (23.0), **5**(25.2), **6**(12.1) and **7**(25.5), which appear at the upfield region compared with that in phenylboronic acid ethanediol ester (31.2).[3] The signal of the boron atom of **6** was observed at the most upfield region among **4**–**7**: the chemical shift of **6** is comparable to that of **1**.[4b] These observations suggest the formation of an intramolecular boron–oxygen coordinate bond in **1**, **4**, **5** and **7** and an intramolecular boron–nitrogen coordinate bond in **6**.

The UV/VIS spectra of **1**, **2** and **4**–**6** in chloroform are summarized in Figure 1. While **1** and **2** show only one band in the longest wavelength region (486 and 414 nm for **1** and **2**, respectively), **4**–**7** show two bands in the longest wavelength absorption regions of **1** and **2**. The relative intensity between these bands in **4**–**7** is lower in the longer wavelength band. Such the difference in shape of the UV/VIS spectra seems to be due to the lowered Lewis acidity of the dioxyboryl groups in **4**–**7** compared with that of the diethylboryl group in **1**. Addition of amine to a solution of **1**, **4**, **5** or **7** in chloroform turns an orange color of the respective solution into yellow one. For example, when an excess (15 equiv.) of *n*-hexyldimethylamine is added, the absorbance of longest wavelength band of **1** is lowered and the new absorption band appears at the corresponding region to the longest wavelength band of **2**. Furthermore, when larger excess of the amine is used, the shape of the longest wavelength absorption band of **1** turns similar to that of **4**. In the ^{1}H NMR spectrum of **1** in $CDCl_3$, the proton signals of chalcone skeleton was observed to shift to upfield region (0.2 ppm) on addition of the amine (15 equiv.). These observations suggest that the dissociation of the intramolecular boron–oxygen coordinate bond takes place by the coordination of *n*-hexyldimethylamine to the boron atom. In contrast, an addition of *n*-hexylamine caused the Michael addition followed by retro aldol-type reaction to give *n*-hexylimines of

Figure 1 UV/VIS spectra of **1**, **2** and **4**–**7** in chloroform

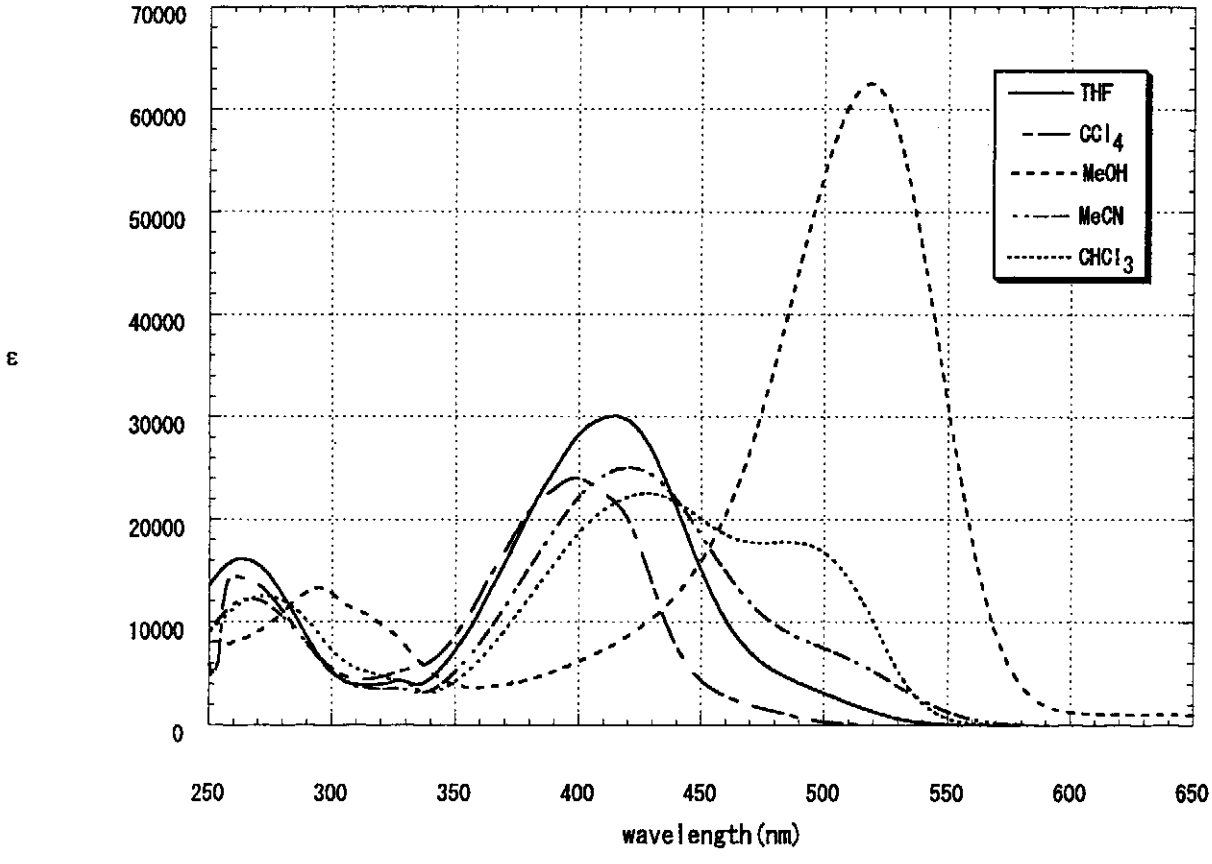


DMAB and 2'-diethylborylacetophenone.

The solvatochromism of the longest wavelength absorption bands is noteworthy. Thus, when the solvent is changed from cyclohexane to methanol a bathochromic shift of 23 nm is observed for **1**, although the dependence of the shift on the solvent polarity is not large.[5] A linear solvation energy relationship (LSER) [$\nu(\mathbf{1}) = 21.55 - 1.692\pi^*$] is obtained between the solvent shifts and the Kamlet–Taft parameter π^*[6] where n = 11, R = 0.948 and σ = 0.139 kK, including both protic and aprotic solvents. A larger bathochromic shift of 33 nm is observed from the same solvent change for **2**.[5] In this case, two separate LSERs [$\nu(\mathbf{2}) = 25.994 - 2.256\pi^*$ and $\nu(\mathbf{2}) = 24.730 - 1.448\pi^*$] are obtained where n = 8, R = 0.931 and σ = 0.263 kK or n = 3, R = 0.995 and σ = 0.012 kK for aprotic or protic solvents, respectively, due to the deviation of the absorption maxima in protic solvent. If the hydrogen-bond donor parameter α is included, the behavior for **2** is described by a single LSER, that is, [$\nu(\mathbf{2}) = 25.924 - 1.933\pi^* - 0.989\alpha$ where n = 11, R = 0.957 and σ = 0.232 kK. In contrast, a very large bathochromic shift of 123 nm is observed for **7** when the solvent is changed from cyclohexane to methanol[7] and, furthermore, the longest wavelength absorption band changes in shape depending on the solvent (Figure 2). The spectrum measured in carbon tetrachloride resemble that in ether in shape and these spectra show one band (λ_{max} 399 and 400 nm, respectively) in the region of the longest wavelength absorption band with tailing (up to 520

nm), which reaches 570 nm in THF, acetone and ethyl acetate. In cyclohexane, acetonitrile, dichloromethane and chloroform two bands appear in the longest wavelength absorption region; the longer wavelength band appears as a shoulder, which is remarkable in chloroform (λ 490 nm). In methanol the longest wavelength absorption band appears bathochromically (λ_{max} 518 nm), whose ε value becomes extremely larger (62500) than those in the other solvents (near 30000). The possibility of decomposition of **7** in methanol is excluded since the UV/VIS spectrum in chloroform of the sample recovered by concentration of the methanol solution is in agreement with that of the newly prepared solution of **7** in chloroform. Furthermore, the ^{1}H NMR spectrum of **7** in methanol-d_4 also did not change even after 1 day at all and no signals due to the methanolysis product a pinacol were detected. When the solvent shifts are plotted against the π^* value in **7** for all the solvents, where the shorter wavelength band in the longest wavelength absorption region is adopted in acetonitrile, dichloromethane and chloroform, the result is unsatisfactory (n = 10, R = 0.452). A good linear relationship is, however, obtained [$\nu(7) = 25.457 - 2.366\pi^*$ where n = 9, R = 0.879 and $\sigma = 0.772$ kK] unless the term of methanol is considered. These findings observed for **7** may be well explained by assuming the presence of an equilibrium based on the dissociation of the intramolecular boron–oxygen coordinate bond depending on the solvent. Thus, according to the kinetic study of 2-[2-(dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-

Figure 2 UV/VIS spectra of **7** in various solvents



dioxaborolane using variable temperature ^{1}H NMR spectra in various solvents reported by Oki,[8] it is revealed that ether, THF and acetone which have affinity toward boron atom promote the dissociation of the intramolecular boron–nitrogen coordinate bond by the solvent assistance and that the dissociation is also promoted in non-polar solvent than in polar solvent since the polarized structure brought about by the intramolecular coordination can not be stabilized in the non-polar solvent. Thus, ether, THF, acetone, ethyl acetate, carbon tetrachloride and cyclohexane promote to shift the equilibrium to the structure without the intramolecular coordination in **7**. In acetonitrile, dichloromethane and chloroform which are polar and possess weak or no coordination ability, the dissociation is somewhat restricted. In contrast, methanol strengthens the intramolecular coordinate bond to promote the polarization of the 4''-dimethylaminochalcone chromophore to shift the equilibrium to the structure bearing the coordination.

Compounds (**1**) and (**2**) are moderately fluorescent and the fluorescence spectra display solvatochromism.[9] Compound (**7**) shows two emission maxima depending on the excitation wavelength, each approximately corresponding to those of **1** and **2**,[10] which supports the presence of the equilibrium derived from the UV/VIS spectral study. For example, when the solvent is changed from ethyl acetate to methanol, bathochromic shifts of 52 and 28 nm are obtained for the shorter and the longer wavelength emission maximum, respectively. In methanol only one emission maximum is observed, which is considered to be the result that the equilibrium is shifted completely to the structure bearing the intramolecular coordinate bond. Compounds (**1**) and (**2**) show good relationships in the Lippert–Mataga equation[11] ($Y = 1.7168 + 3.6745X$ and $Y = 2.8469 + 8.9390X$ where $n = 10$, $R = 0.963$ and $\sigma = 0.0994$ kK or $n = 10$, $R = 0.950$ and $\sigma = 0.282$ kK, respectively), where the difference between the absorption and emission maxima in various solvents are plotted against a measure for solvent polarity defined as $(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 - 1)$. Application of this equation to **7** gives a good relationship for the shifts of the shorter wavelength emission maxima ($Y = 1.1677 + 13.280X$ where $n = 6$, $R = 0.934$ and $\sigma = 0.914$ kK). Similar treatment of **7** for the longer wavelength emission maxima, however, was not successful since the absorption band corresponding to the species bearing the intramolecular boron–oxygen coordinate bond is not assigned in the UV/VIS spectra measured in some solvents, which limits the data needed for the plot of the equation. The shifts of the longer wavelength emission maxima of **7** in various solvents show a good linear relationship with the measure for solvent polarity [$\nu(\mathbf{7}) = 18.712 - 3.839X$ where $n = 7$, $R = 0.798$ and $\sigma = 0.321$ kK] as well as those of the shorter wavelength emission maxima [$\nu(\mathbf{7}) = 22.348 - 11.883X$ where $n = 6$, $R = 0.868$ and $\sigma = 0.880$ kK]. This indicates a more pronounced polarity in the exited state than in the ground state in both cases. Furthermore, as is revealed by the greater value of X coefficient of the latter than that of the former, the intramolecular coordinate bond promotes the polarization of the ground state to reduce the difference of the polarity between the ground state and the exited state.

A single-crystal X-Ray crystallographic study at –120 ℃ reveals the enhanced coplanarity of the skeletal atoms, all the skeletal atoms of **1** being coplanar with a maximum deviation of only 3° (Figure 3), which is different from the structure of **2** where the phenyl group is not coplanar within the molecule (Figure 4). The intramolecular coordinate bond between the boron and oxygen atoms, together with the charge transfer from the dimethylamino group to the carbonyl group, seems to be responsible for the coplanarity. For the comparison of **1** and **2**, the X-Ray structure analysis of **7** was carried out. As shown in Figure 5, the presence of the intramolecular boron–oxygen coordinate bond was confirmed in crystalline state. The intramolecular B1–O1 distance [1.817(5) Å] is, however, longer than that of **1** [1.608(2) Å], which suggests the weakened intramolecular coordinate bond of **7** (Table 1). Furthermore, the THC (tetrahedral character) values of the boron atom[12] in **1** and **7** are estimated to be 52.1 and 36.8%, respectively, which supports the longer B1–O1 distance of **7**. These findings are consistent with the presence of the equilibrium in **7** based on the dissociation of the coordinate bond. The B1 atom is deviated from the plane of the chalcone skeleton [C7–C6–C1–B1 = 5.7(4)°], which reflect the lowered Lewis acidity of the dioxyboryl group. By using the Lippert–Mataga equation and taking the Onsager effective radii estimated from the volume obtained by the X-Ray structure analysis[13] of **2** into account, the difference between the dipole moment vector of the exited state and that of the ground state, $\mu_e - \mu_g$, are calculated to be 5.48 and 8.55 D for **1** and **2**, respectively. Similarly, the values of $\mu_e - \mu_g$ for **7** without the intramolecular coordination is calculated to be 12.8 D if the volume of the molecule is assumed to be constant regardless of dissociation of the coordinate bond. The large value of **7** comparable to that of **2** is consistent with the conclusion deduced from the studies of **1** and **2**, which makes the presence of the equilibrium in **7** more reliable.

EXPERIMENTAL

All reactions were carried out under argon unless otherwise noted. THF, ether, dichloromethane and hexane were distilled from calcium hydride under nitrogen before use. Mps were measured using Yanagimoto micro-melting apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R–250 (250 MHz) or Bruker AVANCE 400S (400 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. ^{11}B NMR spectra were recorded on a Varian GEMINI 2000 (96.3 MHz) using deuteriochloroform as a solvent with boron trifluoride etherate as an internal standard. Electronic spectra were taken with Shimadzu UV–1600PC spectrophotometer. Fluorescence spectra were obtained on a Hitachi 650–60 spectrophotometer. IR spectra were recorded for KBr pellets on a Nicolet FT-IR Impact 410. MS spectra were determined on a Waters LC–MS Integrity System at an ionization potential 70 eV.

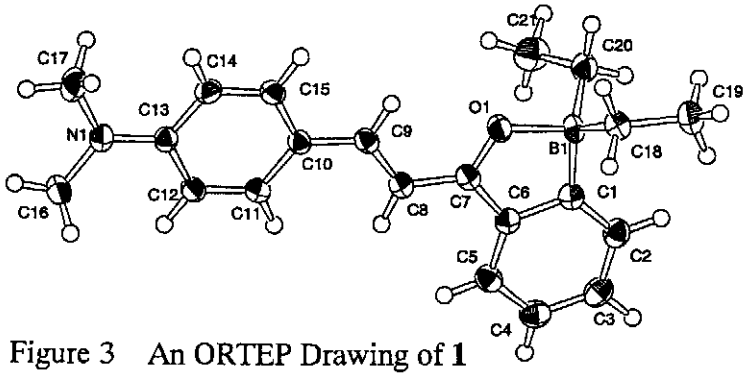


Figure 3 An ORTEP Drawing of **1**

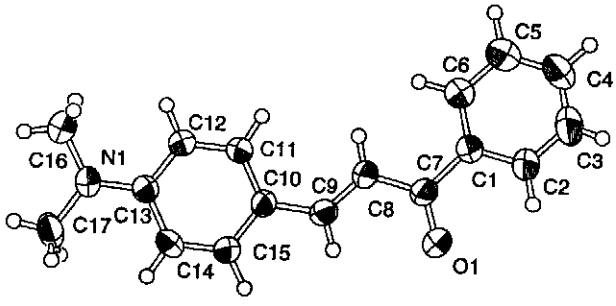


Figure 4 An ORTEP Drawing of **2**

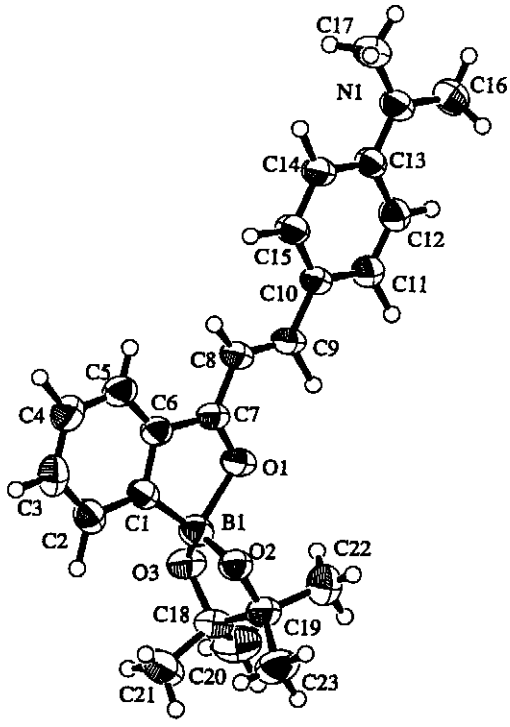


Figure 5 An ORTEP Drawing of **7**

Table 1 Selected bond lengths (Å) and bond angles (°)

	1	**2**	**7**
B1–C1	1.616(3)		1.576(5)
C7–O1	1.294(2)	1.231(4)	1.271(4)
C7–C8	1.424(3)	1.464(4)	1.438(5)
C8–C9	1.367(3)	1.337(4)	1.357(4)
C9–C10	1.434(3)	1.452(4)	1.453(5)
C10–C11	1.411(3)	1.400(4)	1.389(4)
C11–C12	1.372(3)	1.384(4)	1.375(6)
C12–C13	1.420(3)	1.413(4)	1.411(5)
C13–C14	1.412(3)	1.401(4)	1.415(4)
C14–C15	1.372(3)	1,382(4)	1.382(6)
C15–C10	1.405(3)	1.403(4)	1.407(5)
C13–N1	1.359(2)	1.372(4)	1.373(5)
B1–O1	1.608(2)		1.817(5)
O1–B1–C1	97.6(1)		O1–B1–C1 93.8(3)
C20–B1–C18	112.5(2)		O3–B1–O2 109.0(3)
C1–B1–C18	117.6(2)		C1–B1–O3 123.0(3)
C20–B1–C1	113.5(2)		C1–B1–O2 116.4(3)

Synthesis of 2'-Diethylborylacetophenone

Synthesis of acetophenone trimethylsilyl enol ether and its lithiation were carried out according to the reported procedure.[14] To a solution of tetramethylethylenediamine (1.35 mL, 9 mmol) in hexane (10 mL) was added dropwise at ice bath temperature butyllithium (9 mmol) in hexane (5.6 mL) followed by an addition of acetophenone trimethylsilyl enol ether (576 mg, 3 mmol), and the mixture was stirred for 24 h at rt. To a suspension of the lithium compound thus obtained was added at rt a 1.0 M solution of diethylmethoxyborane (6 mmol) in THF (6 mL), and the resulting mixture was stirred for 30 min. The mixture was quenched with brine (10 mL) and the insoluble substances were removed by filtration. The organic layer was separated and concentrated to leave the desired product as a yellow oil (421 mg, 75%), which was used without further purification, δ_H 0.24–0.30 (10H, m), 2.42 (3H, s), 6.91 (1H, t, *J* 7.3), 7.16 (1H, t, *J* 7.3), 7.28 (1H, d, *J* 7.3) and 7.51 (1H, d, *J* 7.3); ν_{max} / cm^{-1} 1600, 1581, 1534, 1455, 1441, 1380 and 1335.

Synthesis of 2'-diethylboryl-4''-dimethylaminochalcone (1)

To a mixture of 2'-diethylborylacetophenone (2.48 g, 13.2 mmol) and 4''-dimethylaminobenzaldehyde (1.97 g, 13.2 mmol) in ether (10 mL) was added at ice bath temperature a solution of LDA (14.5 mmol) prepared from diisopropylamine (1.47 g, 14.5 mmol) and 1.6 M hexane solution of butyllithium (14.5 mmol) in the same solvent (10 mL) and the resulting mixture was stirred for 45 min. The reaction was quenched with brine (10 mL) and the insoluble substances were removed by filtration. The organic layer was separated and concentrated to leave a reddish oily residue, which was purified by chromatography on alumina (benzene as the eluent) followed by crystallization from hexane to give **1** (1.66 g, 39%), mp 84–87 ℃; δ_H 0.65–0.69 (10H, m), 3.11 (6H, s), 6.72 (2H, d, J_{AB} 9.2), 7.30 (1H, t, *J* 7.9), 7.39 (1H, d, J_{AB} 15.3), 7.51 (1H, t, *J* 7.9), 7.66 (2H, d, J_{AB} 9.2), 7.68 (1H, d, *J* 7.3), 8.00 (1H, d, *J* 7.9) and 8.28 (1H, d, J_{AB} 15.3); δ_C 10.1, 14.8, 40.1, 108.6, 111.9, 122.2, 125.1, 125.7, 128.9, 131.9, 132.4, 132.8, 137.9, 150.5, 153.3 and 192.5; δ_B 14.8; ν_{max} / cm^{-1} 1598, 1587, 1558, 1373 and 1173; λ_{max} / nm (log ε) ($CHCl_3$) 288 (4.00) and 486 (4.51); *m/z* 290 (M^+ – Et, 100), 262 (M^+ – 2Et + 1), 162 (51), 131(44) and 98 (67).

Formation of 3

To a mixture of 2'-diethylborylacetophenone (695 mg, 3.7 mmol) and 4''-dimethylaminobenzaldehyde (551 mg g, 3.7 mmol) in benzene and *tert*-butyl alcohol (1:1, 6 mL) was added potassium *tert*-butoxide (457 mg, 4.1 mmol) and the resulting solution was stirred for 3 h. The reaction was quenched with brine (10 mL) and the organic layer was separated and concentrated to leave a reddish oily residue, which was purified by chromatography on alumina (benzene as the eluent) followed by crystallization from benzene to

give **3** (561 mg, 30%), mp 137–138 ℃; δ_H 0.50–0.54 (20H, m), 3.03 (6H, s), 5.30 (2H, s), 6.68 (2H, d, J_{AB}8.6), 7.25–7.38 (3H, m), 7.49 (1H, t, *J* 6.7), 7.58 (1H, s), 7.54–7.61 (2H, m), 7.64 (2H, d, J_{AB}8.6), 8.02 (1H, d, J_{AB}7.9) and 8.16 (1H, d, *J* 7.9); ν_{max} / cm^{-1} 1613, 1567, 1576, 1553, 1533, 1488, 1375, 1167 and 1156; *Anal*. Calcd for $C_{33}H_{41}NO_2B_2$: C, 78.44; H, 8.18; N, 2.77. Found: C, 78.49; H, 8.16; N, 2.74.

Synthesis of 2-[(1',1'-ethylenedioxy)ethyl]benzeneboronic acid

2-[(1',1'-Ethylenedioxy)ethyl]bromobenzene was prepared from the acetalization of 2'-bromo-acetophenone with ethylene glycol in the presence of *p*-toluenesulfonic acid in refluxing benzene. To a solution of the acetal (2.43 g, 10 mmol) in THF (40 mL) was added butyllithium (10 mmol) in hexane (6.3 mL) at –78 ℃ followed by, after 20 min, an addition of triisopropoxyborane (1.88 g, 10 mmol) at this temperature. The reaction mixture was stirred for 1 h, during which time the temperature was raised ambient. The reaction was quenched with brine and the organic layer was separated and concentrated to leave an oily residue. Crystallization from hexane–ethyl acetate (3:1) gave the desired product (1.73 g, 83%), mp 213–215 ℃; δ_H 1.74 (3H, s), 3.86–3.92 (2H, m), 4.05–4.15 (2H, s), 6.37 (2H, br), 7.34 (1H, t, *J* 7.3), 7.41 (1H, t, *J* 7.6), 7.60 (1H, d, *J* 7.9) and 7.91 (1H, *J* 7.3); ν_{max} / cm^{-1} 1600, 1485, 1483, 1354 and 1100; *m*/*z* 193 (M^+ – Me, 78), 149 (42), 121 (38), 98 (34), 87 (100) and 77 (36).

Synthesis of 2'-ethylenedioxyboryl-4''-dimethylaminochalcone (4)

2-[(1',1'-Ethylenedioxy)ethyl]benzeneboronic acid (624 mg, 3 mmol) was dissolved in acetone (10 mL) and *p*-toluenesulfonic acid (5.7 mg, 0.03 mmol) was added to the solution. After stirring for 30 min at rt, the solvent was evaporated to leave an oily residue, which was dried under vacuum. The residue was dissolved in THF–*tert*-butyl alcohol (1:1, 4 mL) and 4''-dimethylaminobenzaldehyde (448 mg, 3 mmol) followed by potassium *tert*-butoxide (1.01 g, 9 mmol) were added at 0 ℃. The resulting solution was stirred for 15 min and the reaction was quenched with brine (4 mL). Yellow precipitate gradually formed and was filtered off and collected (500 mg). The substance was dissolved in methanol (10 mL) and concentrated HCl (5 mL) was added. The resulting violet solution was stirred for 24 h at rt and neutralized with sodium hydrogencarbonate until the evolution of gas ceased. After insoluble substances were filtered off, the filtrate was concentrated to leave a reddish oily residue, which was crystallized from hexane to give **4** (266 mg, 28%), mp 164–165 ℃; δ_H 3.10 (6H, s), 4.34 (4H, s), 6.71 (2H, d, *J* 8.6), 7.33 (1H, d, J_{AB}15.3), 7.44 (1H, t, *J* 7.3), 7,58 (1H, t, *J* 7.3), 7.62 (2H, d, J_{AB}8.6), 7.90 (1H, d, *J* 7.3), 7.93 (1H, d, *J* 7.9) and 8.18 (1H, d, J_{AB}15.3); δ_B 23.0; ν_{max} / cm^{-1} 1590, 1436, 1375, 1171 and 1050; λ_{max} nm (log ε) ($CHCl_3$) 264 (4.08), 431 (3.94) and 500 (4.12, sh); *m*/*z* 321 (M^+, 100), 234 (51), 149 (49), 134 (50) and 77 (47).

Synthesis of 2'-propanedioxyboryl-4''-dimethylaminochalcone (5)

To a solution of **4** (80 mg, 0.25 mmol) in dichloromethane (5 mL) was added 1,3-propanediol (19 mg, 0.25 mmol) and the mixture was stirred for 12 h. The solvent was removed to leave a reddish oily residue, which was dissolved with benzene (3 mL) and washed with brine (3 mL). The organic layer was separated and concentrated to leave an oily residue, which was crystallized from hexane to give **5** (65 mg, 77%), mp 123–125 °C; δ_H 2.14 (4H, m), 3.06 (3H, s), 4.18 (4H, t, *J* 5.5), 6.69 (2H, d, J_{AB}8.6), 7.33 (1H, d, J_{AB}15.3), 7,41 (1H, t, *J* 7.3), 7.51 (1H, t, *J* 7.6), 7.56 (2H, d, J_{AB}8.6), 7.59 (1H, d, *J* 7.6), 7.83 (1H, d, J_{AB}15.3) and 7.87 (1H, d, *J* 7.6)δ_B 25.2; ν_{max} / cm^{-1} 1607, 1593, 1569, 1522, 1435, 1371, 1305, 1259, 1150 and 1125; λ_{max} nm (log ε) ($CHCl_3$) 261 (4.16), 423 (4.19) and 500 (3.49, sh). *Anal*. Calcd for $C_{20}H_{22}NO_3B$: C, 71.66; H, 6.62; N, 4.18. Found; C, 71.20; H, 6.62; N, 3.80.

Synthesis of 6

To a solution of **4** (80 mg, 0.25 mmol) in dichloromethane (5 mL) was added *N*-methydiethanolamine (30 mg, 0.25 mmol) and the mixture was stirred for 12 h. The solvent was removed to leave a reddish oily residue which was dissolved in benzene (5 mL) and washed with brine. The organic layer was separated and concentrated to leave an oily residue which was crystallized from benzene–hexane (1:1) to give crude **6.** Recrystallization from hexane–2-propanol (10:1) afforded pure **6** (67 mg, 71%); δ_H 2.59 (3H, s), 2.99 (6H, s), 3.16 (4H, br t), 4.03 (4H, br t), 6.62 (2H, d, *J* 8.6), 6.80 (1H, d, J_{AB}15.3), 7.15–7.20 (2H, m), 7,26–7.34 (2H, m), 7.37 (2H, d, J_{AB}8.6) and 7.80 (1H, d, *J* 7.3); δ_B 12.1; ν_{max} / cm^{-1} 1632, 1595, 1525, 1368, 1184, 1171 and 1115; λ_{max} nm (log ε) ($CHCl_3$) 275 (4.12), 429 (4.42) and 500 (3.78, sh); *m*/*z* 378 (M^+, 2), 278 (35), 262 (27), 247 (48) and 88 (100).

Synthesis of 7

To a solution of **4** (80 mg, 0.25 mmol) in dichloromethane (5 mL) was added pinacol (30 mg, 0.25 mmol) and the mixture was stirred for 12 h. The solvent was removed to leave a reddish oily residue which was crystallized from hexane–ethyl acetate (3:1) to give **7** (68 mg, 72%), mp 175–176 °C; δ_H 1.42 (12H, s), 3.05 (6H, s), 6.69 (2H, d, *J* 8.6), 7.28 (1H, d, J_{AB}15.3), 7.41 (1H, t, *J* 7.6), 7.53 (1H, t, *J* 7.6), 7.56 (2H, d, J_{AB}8.6), 7.63 (1H, d, *J* 7.6), 7.86 (1H, d, *J* 7.6) and 7.93 (1H, d, J_{AB}15.3); δ_B 25.5; ν_{max} / cm^{-1} 1603, 1591, 1569, 1526, 1505, 1437, 1299, 1184, 1167, 1123 and 1032 ; λ_{max} nm (log ε) ($CHCl_3$) 273 (4.09), 428 (4.33) and 486 (4.22, sh). *Anal.* Calcd for $C_{23}H_{28}NO_3B$: C, 73.22; H, 7.48; N, 3.71. Found: C, 73.02; H, 7.48; N, 3.63.

Reaction of 1 with *n*-hexylamine

To a solution of **1** (80 mg, 0.25 mmol) in dichloromethane (5 mL) was added *n*-hexylamine (101 mg, 1

mmol) and the mixture was stirred for 12 h. The solvent was removed to to leave an oily residue whose ^{1}H NMR spectrum showed the presence of *n*-hexylimines of 4-dimethylaminobenzaldehyde and 2'-diethylborylacetophenone. Purification by column chromatography on silica gel (hexane–ethyl acetate; 5:1) afforded 4-dimethylaminobenzaldehyde and *n*-hexylimine of 2'-diethylborylacetophenone in 75 and 70 % yields, respectively, imine: oil (47 mg), δ_H 0.41–0.47 (8H, m), 0.70–0.72 (2H, m), 0.91–0.94 (3H, m), 1.34–1.41 (6H, m), 1.54–1.67 (2H, m), 2.51 (3H, s), 3.54–3.58 (2H, m), 7.22 (1H. dt, *J* 7.5 and 1.1), 7.39 (1H, dt, *J* 7.2 and 1.0), 7.59 (1H, d, *J* 7.5) and 7.61 (1H, d, *J* 7.7).

X-Ray structure analysis of 1, 2 and 7

Data were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo–Kα radiation (λ = 0.71069 Å) and a rotating anode generator. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Crystal data for **1**: $C_{21}H_{26}NOB\bullet1.5C_6H_6$, M = 436.42, red, prismatic crystal (0.20 × 0.40 × 0.80 mm), triclinic, *P*1 (#2), *a* = 9.622(4), *b* = 15.155(5), *c* = 9.522(3) Å, *α* = 101.21(3), *β* = 95.90(4), *γ* = 108.32(3)°, *U* = 1272.9(9) Å^3, *Z* = 2, D_c = 1.139 gcm^{-3}, *μ* = 0.67 cm^{-1}, *F*(000) = 470, *T* = 153 K The final cycle of full-matrix least squares refinement was based on 3338 observed reflections [$I > 3.00\ \sigma(I)$] and 438 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.040 and *R*w = 0.046. Crystal data for **2**: $C_{17}H_{17}NO$, M = 251.33, yellow, prismatic crystal (0.20 × 0.40 × 0.60 mm), monoclinic, $P2_1/a$ (#14), *a* = 9.491(4), *b* = 11.884(3), *c* = 12.912(3) Å, *β* = 108.35(2)°, *U* = 1382.3(7) Å^3, *Z* = 4, D_c = 1.208 gcm^{-3}, *μ* = 0.75 cm^{-1}, *F*(000) = 536, *T* = 153 K The final cycle of full-matrix least squares refinement was based on 1347 observed reflections [$I > 3.00\ \sigma(I)$] and 241 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.051 and *R*w = 0.065. Crystal data for **7**: $C_{23}H_{28}BNO_3$, M = 377.29, red, prismatic crystal (0.42 × 0.20 × 0.14 mm), monoclinic, $P2_1/c$ (#14), *a* = 9.886(5), *b* = 18.978(7), *c* = 11.735(6) Å, *β* = 108.56(4)°, *U* = 2086(1) Å^3, *Z* = 4, D_c = 1.201 gcm^{-3}, *μ* = 0.78 cm^{-1}, *F*(000) = 808, *T* = 295 K The final cycle of full-matrix least squares refinement was based on 1807 observed reflections [$I > 3.00\ \sigma(I)$] and 254 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.058 and *R*w = 0.077.

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5 Solvatochromism in the longest wavelength absorption bands of **1** and **2** (nm): cyclohexane (464, 386), Et_2O (478, 390), CCl_4 (468, 394), Pr^iOH (481, 416), EtOH (486, 418), AcOEt (486, 402), THF (490, 405), MeOH (487, 419), MeCN (494, 408), $CHCl_3$ (486, 414), CH_2Cl_2 (492, 414).

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9 Solvatochromism of the fluorescence of **1** and **2** (nm): cyclohexane (512, 449), Et_2O (533, 465), CCl_4 (512, 449), Pr^iOH (559, 542), EtOH (562, 545), AcOEt (552, 493), THF (559, 485), MeOH (563, 546), MeCN (576, 530), $CHCl_3$ (546, 505), CH_2Cl_2 (559, 520).

10 Solvatochromism of the fluorescence of **7** (nm): AcOEt (490, 560), Me_2CO (518, 570), THF (498, 555), MeCN (542, 560), CH_2Cl_2 (521, 562), $CHCl_3$ (490, 550), MeOH (578).

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