

B₃O₃Ph₃(7-azaindole): Structure, Luminescence, and Fluxionality

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Received January 27, 1999

Summary: A 7-azaindole adduct of boroxine, B₃O₃Ph₃-(7-azaindole), **1**, was obtained from the reaction of PhB(OH)₂ with 7-azaindole. The crystal structure of **1** shows that the 7-azaindole ligand is bonded to the boroxine molecule through a B–N bond and an H···O hydrogen bond. Compound **1** is fluorescent in solution and the solid state. There is, however, a dramatic difference in the emission maximum of the solution ($\lambda_{\text{max}} = 368 \text{ nm}$) and solid ($\lambda_{\text{max}} = 400 \text{ nm}$) spectra. The solution behavior of **1** was examined by ¹H NMR spectroscopic methods, which established that compound **1** is highly fluxional in solution, attributable to an intermolecular 7-azaindole ligand dissociation/association process with an activation energy of $34 \pm 1.5 \text{ kJ mol}^{-1}$. To determine the role of the hydrogen bond in the dynamic process of **1**, the structure and solution behavior of B₃O₃Ph₃(Py), **2**, was also examined. In solution compound **2** undergoes an intermolecular exchange process similar to that of compound **1**, with an activation energy of $39 \pm 1.5 \text{ kJ mol}^{-1}$. The relatively small activation energy in **1** could be attributed to the hydrogen bond and the reduced base strength of 7-azaindole, relative to that of pyridine.

Introduction

We reported recently that 7-azaindole is a good blue emitter when bound to aluminum or boron centers.^{1,2} The usefulness of 7-azaindole boron compounds in electroluminescence has been demonstrated by a blue electroluminescent device using our boron compound B₂-(O)(7-azain)₂R₂, R = ethyl or phenyl, as the emitting layer.^{2b} In search of new luminescent boron compounds, we initiated the investigation on 7-azaindole derivatives of boroxines. The attractiveness of boroxines lies in the fact that they are generally stable chemically and thermally,³ making them potentially good candidates for electroluminescent applications. Although boronic acids that contain an aromatic fluorophore have been found recently to be effective as fluorescent probes,⁴ the

luminescent properties of boroxine-based compounds in the visible region have not been investigated. We therefore report a new 7-azaindole compound, B₃O₃Ph₃-(7-azaindole) (**1**), which is not only luminescent but also highly fluxional in solution. The synthesis, structure, luminescence, and fluxionality of **1** are presented herein.

Experimental Section

All syntheses were carried out under a nitrogen atmosphere. Solvents were freshly distilled prior to use. 7-Azaindole and PhB(OH)₂ were purchased from Aldrich Chemical Co. NMR spectra were recorded on a Bruker AM 400 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, British Columbia. Excitation and emission spectra were recorded on a Photon Technologies International QM1 spectrometer.

Syntheses. B₃O₃(Ph)₃(7-azain) (1**).** 7-Azaindole (0.118 g, 1 mmol) was added to phenylboron dihydroxide (0.366 g, 3 mmol) in 10 mL of toluene at 23 °C. The mixture was stirred and heated at 80 °C for 5 h. After the solution was cooled to room temperature, it was concentrated to about 2 mL by vacuum. After the solution was kept for several days at 23 °C, colorless crystals of compound **1** were obtained. Yield: 0.28 g (65%). ¹H NMR (CD₂Cl₂, ppm, 25 °C): δ 10.52 (s, 1H, 7-azain), 8.85 (d, ³J = 5.7 Hz, 1H, 7-azain), 8.24 (d, ³J = 7.7 Hz, 1H, 7-azain), 8.02 (dd, ³J = 6.8 Hz, ⁴J = 3.4 Hz, 6H, Ph), 7.47 (d, ³J = 3.6 Hz, 1H, 7-azain), 7.40–7.38 (m, 9H, Ph), 7.36 (t, ³J = 6.8 Hz, 1H, 7-azain), 6.65 (d, ³J = 3.6 Hz, 1H, 7-azain). ¹³C NMR (CD₂Cl₂, ppm, 25 °C): δ 136.61 (7-azain), 134.42 (7-azain), 133.77 (Ph), 130.09 (Ph), 127.99 (Ph), 127.10 (7-azain), 116.19 (7-azain), 102.41 (7-azain). ¹¹B NMR (CDCl₃/CH₂Cl₂, 400 MHz, ppm, relative to BF₃·O(C₂H₅)₂, 25 °C): δ 20.53 (s, 3B). Anal. Calcd for C₂₅H₂₁N₂O₃B₃: C, 69.84; H, 4.92; N, 6.52. Found: C, 69.64; H, 4.93; N, 6.50.

B₃O₃(Ph)₃(Pyr) (2**).** Compound **2** was obtained by a procedure similar to that for compound **1** in 56% yield. ¹H NMR (CD₂Cl₂, ppm, 25 °C): δ 9.07 (dd, ³J = 6.6 Hz, ⁴J = 1.5 Hz, 2H, Pyr), 8.07 (³J = 6.1 Hz, ⁴J = 2.5 Hz, 6H, Ph), 8.01 (tt, ³J = 7.7 Hz, ⁴J = 1.5 Hz, 1H, Pyr), 7.63 (t, ³J = 7.5 Hz, 2H, Pyr), 7.43–7.39 (m, 9H, Ph). ¹³C NMR (CD₂Cl₂, 400 MHz, ppm, 25 °C): δ 143.87 (Pyr), 140.76 (Pyr), 133.76 (Ph), 129.74 (Ph), 127.55 (Ph), 125.54 (Pyr). ¹¹B NMR (CDCl₃/CH₂Cl₂, 400 MHz, ppm, relative to BF₃·O(C₂H₅)₂, 25 °C): δ 20.47 (s, 3B). Anal. Calcd for C₂₃H₂₀N₂O₃B₃: C, 70.68; H, 5.16; N, 3.58. Found: C, 70.53; H, 5.10; N, 3.62.

X-ray Diffraction Analyses. All crystals were obtained from concentrated toluene solutions and mounted on glass capillaries. All data were collected on a Siemens P4 single-crystal diffractometer with graphite-monochromated Mo K α radiation, operated at 50 kV and 40 mA at 23 °C. The data for **1** were collected over 2θ 3–50°, while the data for **2** were collected over 2θ 3–48°. Three standard reflections were measured every 197 reflections. No significant decay was

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(3) (a) Washburn, R. M.; Levens, E.; Albright, C. F.; Billig, F. A. *Org. Synth.* **1959**, *39*, 3. (b) Snyder, H. R.; Konecky, M. S.; Lennarz, W. J. *J. Am. Chem. Soc.* **1958**, *80*, 3611. (c) Brown, H. C.; Cole, T. E. *Organometallics* **1985**, *4*, 816. (d) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; pp 202–203.

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Table 1. Crystallographic Data

	1	2
formula	C ₂₅ H ₂₁ N ₂ O ₃ B ₃	C ₂₃ H ₂₀ NO ₃ B ₃
fw	429.9	390.8
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	11.8267(11)	14.671(4)
<i>b</i> /Å	14.243(2)	11.562(8)
<i>c</i> /Å	13.7878(12)	13.062(7)
α /deg	90	90
β /deg	100.272(4)	103.65(3)
γ /deg	90	90
<i>V</i> /Å ³	2285.4(5)	2153(2)
<i>Z</i>	4	4
<i>D</i> _c , g cm ⁻³	1.25	1.21
μ , cm ⁻¹	0.80	0.77
2 θ _{max} , deg	50	48
reflins measured	4275	3509
reflins used (<i>R</i> _{int})	4008 (0.040)	3341 (0.024)
no. of variables	299	271
final <i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a = 0.0675 <i>wR</i> ₂ ^b = 0.1235	<i>R</i> ₁ = 0.0574 <i>wR</i> ₂ = 0.1344
<i>R</i> (all data)	<i>R</i> ₁ = 0.1910 <i>wR</i> ₂ = 0.1806	<i>R</i> ₁ = 0.0858 <i>wR</i> ₂ = 0.1585
goodness-of-fit on <i>F</i> ²	1.009	1.099

^a *R*₁ = $\sum |F_o| - |F_c| / \sum |F_o|$. ^b *wR*₂ = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.
 $w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

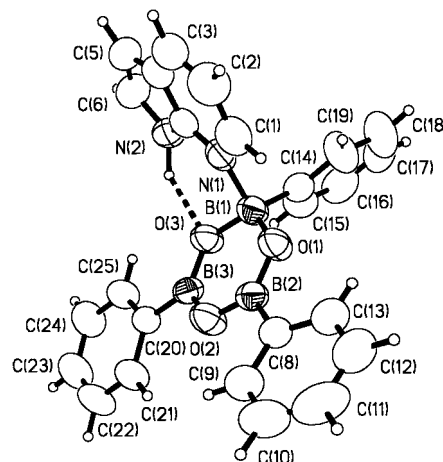
observed for either crystal during the data collection. Data were processed on a Pentium PC using Siemens SHELXTL software package (version 5.0)⁵ and corrected for Lorentz and polarization effects. Neutral atom scattering factors were taken from Cromer and Waber.⁶ The crystals of **1** and **2** belong to the monoclinic crystal system. The space groups *P*2₁/*n* and *P*2₁/*c* were determined uniquely for compounds **1** and **2**, respectively, on the basis of systematic absences. The structures were solved by direct methods. The positions for all hydrogen atoms were calculated, and their contributions in structural factor calculation were included. All non-hydrogen atoms in **1** and **2** were refined anisotropically. The crystallographic data for compounds **1** and **2** are given in Table 1.

Results and Discussion

Structure of **1** in the Solid State and in Solution.

Our initial intention in carrying out the reaction of PhB(OH)₂ with 7-azaindole was to make new boron complexes where the 7-azaindole anion (7-azain) functions as a bridging ligand in a manner similar to that in R₂B₂(O)(7-azain)₂ compounds.² However, regardless of the reaction conditions and the amount of 7-azaindole used, we found that compound **1** with the formula of B₃O₃(Ph)₃(7-azain-H) was always obtained as the only product. Compound **1** can be regarded as a 7-azaindole adduct of the boroxine compound B₃O₃Ph₃. The formation of the boroxine compound from the reaction of PhB(OH)₂ is not surprising because it has been well established that RB(OH)₂ can cyclize readily to form the corresponding boroxine compound when either heated or Lewis bases are present in solution.³ Compound **1** displays an unusual purple luminescence in the solid state when irradiated by UV light. In solution, it appeared to be highly dynamic. To fully understand the properties of compound **1**, we determined the structure of **1** by a single-crystal X-ray diffraction analysis.

The molecular structure of **1** is shown in Figure 1. Selected bond lengths and angles are given in Table 2.

**Figure 1.** Diagram showing the molecular structure of **1** with 50% thermal ellipsoids and labeling schemes.**Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1****

O(2)–B(2)	1.372(6)	O(1)–B(1)	1.456(6)
O(2)–B(3)	1.383(5)	N(1)–B(1)	1.666(7)
O(3)–B(3)	1.348(5)	C(14)–B(1)	1.580(7)
O(3)–B(1)	1.478(6)	C(20)–B(3)	1.547(6)
O(1)–B(2)	1.345(5)	C(8)–B(2)	1.548(6)
B(2)–O(2)–B(3)	121.5(4)	O(2)–B(3)–C(20)	118.5(4)
B(3)–O(3)–B(1)	122.8(4)	O(1)–B(1)–O(3)	112.5(4)
B(2)–O(1)–B(1)	123.0(4)	O(1)–B(1)–C(14)	113.8(4)
O(1)–B(2)–O(2)	120.3(4)	O(3)–B(1)–C(14)	113.1(4)
O(1)–B(2)–C(8)	120.8(5)	O(1)–B(1)–N(1)	103.5(4)
O(2)–B(2)–C(8)	118.9(4)	O(3)–B(1)–N(1)	104.6(4)
O(3)–B(3)–O(2)	119.5(4)	C(14)–B(1)–N(1)	108.3(4)
O(3)–B(3)–C(20)	122.0(4)		

The basic features of the structure of **1** resemble those of previously known B₃Ph₃(O)₃L compounds, where L is a simple Lewis donor.⁷ Two of the boron atoms (B(2), B(3)) have a trigonal planar geometry while the third boron atom (B(1)) has a tetrahedral geometry. The B(2)–O(2), B(2)–O(1), B(3)–O(3), and B(3)–O(2) distances ranging from 1.345(5) to 1.383(5) Å are much shorter than those of B(1)–O(1) and B(1)–O(3) (1.456(6), 1.478(6) Å), consistent with the geometry around each boron center. Similarly, the B(2)–C(8) and B(3)–C(20) bond lengths (1.548(6), 1.547(6) Å) are somewhat shorter than that of B(1)–C(14) (1.580(7) Å). The B(1)–N(1) bond length (1.666(7) Å) is similar to those previously reported.⁷ However, unlike the previously reported structures of B₃Ph₃(O)₃L where no internal hydrogen bonds are present, the 7-azaindole ligand in **1**, in addition to the formation of a B–N bond, forms an internal hydrogen bond⁸ with the oxygen atom, O(3), as evident by the distance of N(2)···O(3), 2.792 Å. Niedenzu and Bielawski reported a pyrazole adduct,^{9a} B₃O₃Ph₃(Hpz), in 1986. Two different structures were proposed for B₃O₃Ph₃(Hpz) by Niedenzu's and Yalpani's groups,^{9a,b} on the basis of their solution NMR studies.

(7) (a) Yalpani, M.; Boese, R. *Chem. Ber.* **1983**, *116*, 3347. (b) Beckett, M. A.; Strickland, G. C.; Varma, K. S. *Polyhedron* **1995**, *14*, 2623. (c) Beckett, M. A.; Strickland, G. C.; Varma, K. S.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *J. Organomet. Chem.* **1997**, *535*, 33.

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(5) SHELXTL crystal structure analysis package, Version 5; Bruker Axs, Analytical X-ray System: Madison, WI, 1995.

(6) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, Al, 1974; Vol. 4, Table 2.2A.

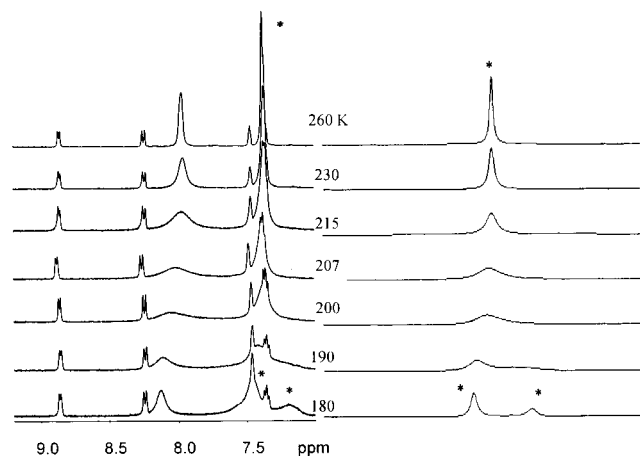


Figure 2. Variable-temperature ^1H NMR spectra of **1** in CD_2Cl_2 (left) and the simulated spectra for the phenyl chemical shift at 7.39 ppm (right).

We believe that it is very likely that in the solid state Niedenzu's compound has a hydrogen bond structure similar to that of **1**.

Due to the formation of the hydrogen bond, each of the three boron atoms in **1** in the solid state has a distinct environment. In solution, one can anticipate that the hydrogen bond could switch rapidly between O(3) and O(1), resulting in a similar chemical environment for both B(2) and B(3). Hence, chemical shifts due to two types of phenyl groups should be observed in the ^1H and ^{13}C NMR spectra of **1** in solution. However, contrary to our anticipation, only one set of chemical shifts due to phenyls was observed in ^1H and ^{13}C NMR spectra of **1** at ambient temperature, indicating that compound **1** must be fluxional in solution. Variable-temperature ^1H and ^{13}C NMR confirmed the presence of a dynamic process. As shown in Figure 2, the two peaks at 8.02 (protons at 2,6 positions) and 7.39 ppm (protons at 3, 4, 5 positions, marked by *) due to the phenyl groups broaden as the temperature decreases. At 180 K, two broad peaks with a 2:1 ratio due to the protons at 3, 4, 5 positions were observed, which is in agreement with the presence of two types of phenyl environments.

There are two possible mechanisms responsible for the dynamic behavior of **1**. The first mechanism involves an intramolecular migration of the 7-azaindole to all three boron sites. The second mechanism is an intermolecular process involving the dissociation of the 7-azaindole ligand from **1** and the reattachment of 7-azaindole ligand to the boroxine $\text{B}_3\text{O}_3\text{Ph}_3$, averaging the environment around the three boron centers. If the exchange process is an intramolecular process, the chemical shifts of the coordinated 7-azaindole ligand should not be affected by the presence of free 7-azaindole ligand in solution. Consequently two sets of 7-azaindole chemical shifts, the coordinated ones and the uncoordinated ones, should be observed in the NMR spectra of the mixture of **1** and 7-azaindole. To distinguish between the intra- and intermolecular exchange mechanisms, we examined a series ^1H NMR spectra of **1** in the presence of varied amount of 7-azaindole. The ^1H NMR spectra of the solution of **1** and 7-azaindole from a 1:0 ratio to a 1:8 ratio were examined. Only one set of chemical shifts due to 7-azaindole was observed, regard-

Scheme 1

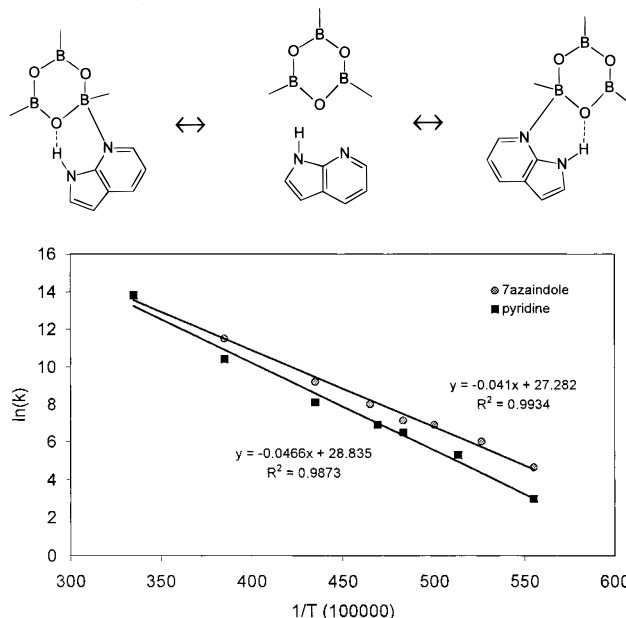


Figure 3. Diagram showing the plot of $\ln(k)$ vs $1/T$ and the linear fit for compounds **1** and **2**.

less of the ratio of **1** and noncoordinated 7-azaindole, indicative of the presence of a rapid exchange between coordinated and noncoordinated 7-azaindole ligands. In addition, the NMR spectra show that as the concentration of 7-azaindole increases in solution, the chemical shifts due to 7-azaindole shift toward those of free 7-azaindole, further supporting the presence of the intermolecular exchange process shown in Scheme 1. Because the exchange process of **1** is between two nonequally populated sites (one tetrahedral boron site and two trigonal planar boron sites), the free energy for the exchange process therefore cannot be obtained by using $k = 2.22 \Delta\nu$ and the Eyring equation.¹⁰ We therefore performed a line shape analysis¹⁰ for the phenyl peak located at 7.39 ppm in the ^1H NMR spectra of **1** over the temperature range 260–180 K. The simulated spectra are shown in Figure 2. From the data of line shape analyses, we obtained the exchange rate k for several temperatures. From the slope of the plot of $\ln(k)$ versus $1/T$ the activation energy E_a of 34 ± 1.5 kJ mol^{-1} was obtained (Figure 3).

A similar dynamic process was also observed in $\text{B}_3\text{R}_3\text{O}_3\text{L}$, where L is a simple terminal ligand.⁷ A quantitative kinetic analysis on some of the previously known $\text{B}_3\text{R}_3\text{O}_3\text{L}$ compounds was reported by Beckett and co-workers.^{7b,c} However, in their analysis, the equation $k = 2.22 \Delta\nu$ was used in the calculation of the exchange rate constant and the subsequent derivation of free energy, which is in error because the exchange is not on two equally populated sites.

To compare the exchange behavior of **1** with that of simple Lewis base adducts, $\text{B}_3\text{R}_3\text{O}_3\text{L}$, we synthesized $\text{B}_3\text{R}_3\text{O}_3(\text{Py})$ (**2**). The structure¹¹ of **2** is very similar to those of $\text{B}_3\text{R}_3\text{O}_3\text{L}$ molecules reported earlier. The solution behavior of **2** is very similar to that of **1**, i.e., a rapid

(10) Günther, H. *NMR Spectroscopy*, 2nd ed.; John Wiley & Sons: Chichester, 1992.

(11) The detail of the structure of **2** can be found in the Supporting Information.

dissociation/coordination of pyridine. The line shape analysis for the phenyl peak at 7.41 ppm in the variable-temperature ^1H NMR data established that the activation energy for the exchange process of **2** is 39 ± 1.5 kJ mol $^{-1}$. The fact that the activation energy for the exchange process of $\text{B}_3\text{R}_3\text{O}_3(\text{Py})$ is lower than that of $\text{B}_3\text{R}_3\text{O}_3(7\text{-azaindole})$ is somewhat surprising because 7-azaindole is a much bigger ligand than pyridine; hence one would expect the exchange process for **1** could be slower and the activation energy would be higher than that of **2**. The activation energy discrepancy between **1** and **2** could be explained by an intermediate involving a hydrogen bond in the exchange process of **1** which effectively decreases the energy barrier for compound **1**, in comparison to that of compound **2**, where such an intermediate is not possible. The alternative explanation is that 7-azaindole is a weaker base than pyridine due to both steric and electronic factors, resulting in a relatively low activation energy in compound **1**.

Luminescence of 1. The free 7-azaindole ligand and compound **2** have no emission in the visible region in both solution and solid state. We have demonstrated previously that the coordinated 7-azaindole anion does produce blue luminescence in aluminum and boron complexes.^{1,2} Because the 7-azaindole ligand in **1** is neutral, we did not anticipate any emission by this compound in the visible region. It is therefore to our surprise when we observed that compound **1** emits a purple color when irradiated by UV light in the solid state. The emission maximum of **1** in the solid state was determined to be at $\lambda = 400$ nm. The formation of a hydrogen bond and a B–N bond between the 7-azaindole and the $\text{B}_3\text{Ph}_3\text{O}_3$ unit must have played an important role in promoting the luminescence because a similar luminescence has not been observed in complexes where 7-azaindole coordinates to Al(III) or B(III) as a terminal ligand through the pyridyl nitrogen site only.¹² An interesting phenomenon is the blue shift of the emission band in solution, as shown in Figure 4.

The emission maximum of **1** in solution is at $\lambda = 365$ nm, very close to that of free 7-azaindole ligand in

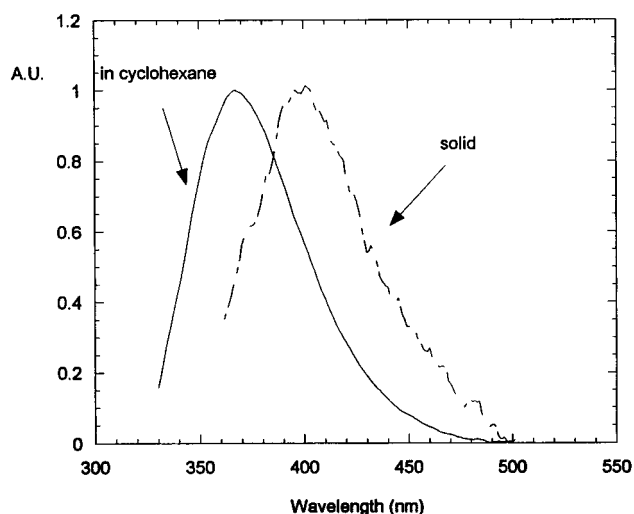


Figure 4. Emission spectra of compound **1** in solution (dashed line) and solid state (solid line).

solution ($\lambda = 357$ nm). Based on our NMR studies of the solution behavior of **1**, the blue shift of the emission band in solution can be attributed to the dissociation/coordination exchange process of the 7-azaindole ligand. The emission band in solution therefore contains contributions from both compound **1** and the free 7-azaindole ligand. Compound **1** is stable in air and can be sublimed readily at 110 °C and 0.08 mmHg, making it a potential candidate for applications in organic electroluminescent devices, which is being investigated in our laboratory.

Acknowledgment. We thank the Natural Science and Engineering Research Council of Canada for financial support.

Supporting Information Available: Crystal data, tables of atomic coordinates, thermal parameters, a complete list of bond lengths and angles, hydrogen parameters, and a diagram showing the structure of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM990053T

(12) Wu, Q. and Wang, S. Unpublished results.