# OPTICALLY DETECTED MAGNETIC RESONANCE STUDY OF THE PHOSPHORESCENT STATES OF BBr₃ COMPLEXES OF PYRIDINE AND ISOQUINOLINE

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## Summary

The phosphorescence spectra, lifetimes and zero-field splitting parameters of the triplet state of $BBr_3$ complexes with pyridine and isoquinoline are reported. These results are compared with values obtained for the corresponding protonated azines. For pyridine we find a substantial decrease in both the phosphorescence lifetime and the zero-field splitting parameter $D$ for the $BBr_3$ complex in comparison with the protonated species. For isoquinoline these changes are not so great. We explain these results in terms of inductive and mesomeric effects on the pyridine triplet, from the complexed $BBr_3$. For isoquinoline such effects seem to be less important.

## 1. Introduction

Pyridine has been shown to phosphoresce when complexed to a Lewis acid, such as a proton or a boron trihalide [1]. In pyridine protonation lowers the zero-field splitting (ZFS) parameter $D$ relative to the unprotonated (non-phosphorescent) azine [2], and this trend is also observed for other azines [3, 4]. There have been various mechanisms proposed in the literature to explain the changes in $D$. While Kwiram and coworkers [2, 5] state that such effects can be explained solely on the basis of spin–spin interactions without invoking the mixing of $^3\pi–\pi^*$ and $^3n–\pi^*$ states, Chodkowska *et al.* [3] suggest that vibronic mixing of $n–\pi^*$ and $\pi–\pi^*$ states is responsible for the lowering of $D$.

In the present work, we investigate the effects of complexing the Lewis acid $BBr_3$ on the phosphorescence properties and the ZFS parameters of pyridine and the related azine, isoquinoline, in an effort to elucidate a model for the role that the Lewis acid plays in determining the triplet state properties of these complexes. It appears that for pyridine and isoquinoline, the phosphorescent state of the $BBr_3$ complex can be described

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in terms of substituent effects on the ring system from the complexed Lewis acid, which exerts an inductive and mesomeric effect which can perturb the phosphorescent triplet state [6]. While for pyridine these mesomeric and inductive effects are large, for isoquinoline such mesomeric and inductive contributions seem to be less important and the triplet state of the $BBr_3$ complex is very similar to that of the protonated species.

## 2. Experimental details

The complexes of pyridine and isoquinoline with $BBr_3$ were prepared under nitrogen, following published procedures, as crystalline compounds and were analyzed via IR and mass spectroscopy [7]. Protonated isoquinoline was prepared by bubbling HCl gas through an ether solution of isoquinoline and recrystallizing the precipitate from ethanol.

The samples were excited with a 100 W mercury lamp, whose output was passed through a saturated $NiSO_4$ solution filter and a Corning 7-54 glass filter. Phosphorescence at 77 K was isolated by means of a rotating slotted disc phosphorimeter, dispersed through a 0.75 m Jarrell Ash monochromator and detected photoelectrically. For the measurement of phosphorescence decays, the sample was excited at right angles to the direction of observation, and synchronously linked mechanical shutters in the excitation and observation directions were utilized to initiate decay and to minimize detection of scattered light. Multiple decay curves were accumulated on a signal averager to enhance the signal-to-noise ratio. Additional experimental details have been reported previously [8].

The ZFS parameters were determined in polycrystalline samples of the neat compounds at 2 K via amplitude-modulated optically detected magnetic resonance (ODMR) [9]. In our ODMR experiment, the microwave sweep oscillator, amplified to 1 W by a Hughes 1403H solid state amplifier, was square wave amplitude modulated by a General Microwave DM864 PIN diode switch. The phosphorescence was observed at right angles and was phase sensitive detected at the modulation frequency with a Princeton Applied Research model 126 lock-in amplifier. Signal averaging was used to enhance the signal-to-noise ratio.

## 3. Results and discussion

Phosphorescence spectra of the $BBr_3$ complexes in $n$-butyl alcohol glass at 77 K are shown in Figs. 1 and 2, together with spectra for the protonated and uncomplexed azine. Pyridine–$BBr_3$ (py–$BBr_3$) gives a broad structureless spectrum with a maximum at 439 nm. This phosphorescence is similar in appearance to the $BCl_3$ complex reported by Snyder and Testa [1], which had a phosphorescence maximum at 420 nm. On protonation or complexation to $BBr_3$ the phosphorescence of isoquinoline shows a red
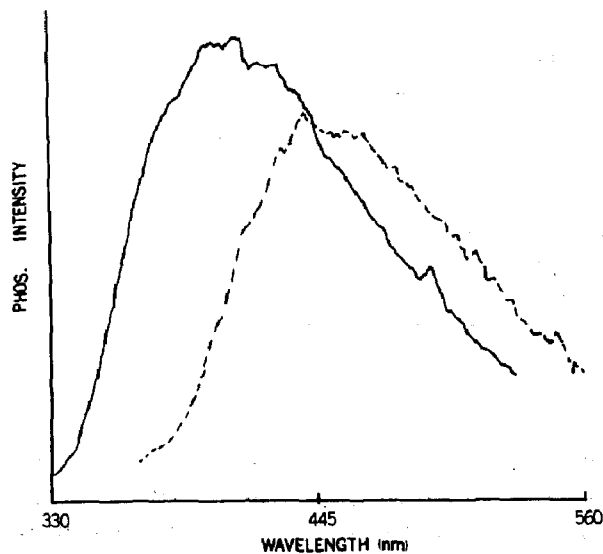
Fig. 1. Phosphorescence spectra in *n*-butyl alcohol of pyridine complexed to BBr₃
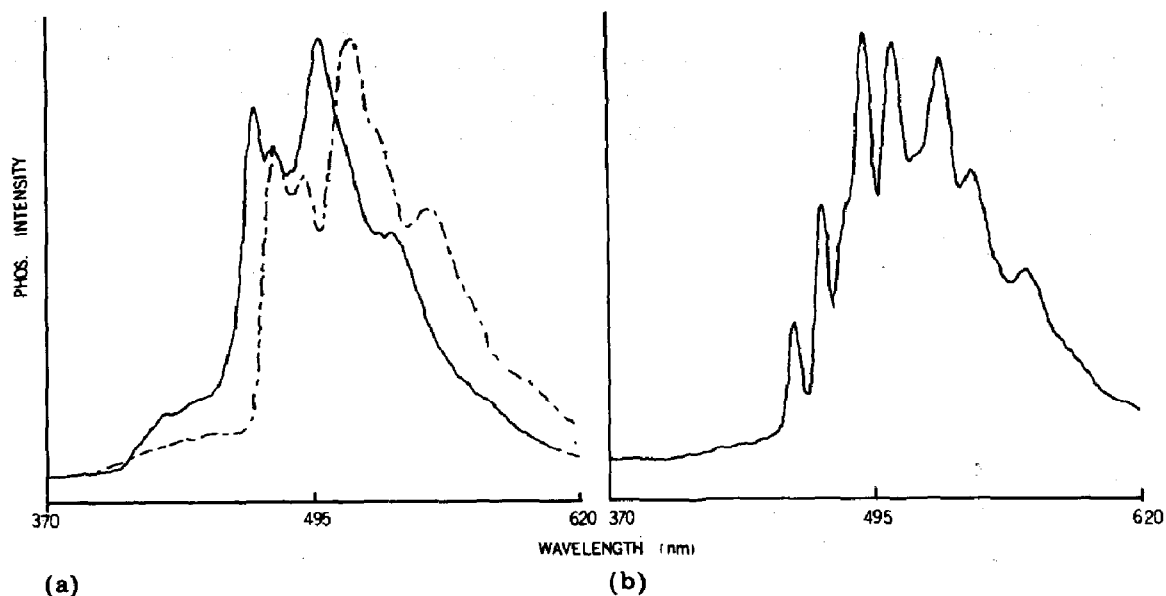(— — —) and pyridine–HCl (————).



(a)                                        (b)

Fig. 2. (a) Phosphorescence spectra of isoquinoline complexed to BBr₃ (————) and
isoquinoline–HCl (— — —) in *n*-butyl alcohol solvent; (b) phosphorescence of isoquinoline
in the same solvent.

shift of 31 nm or 6 nm respectively. Both complexes show similar vibronic
structure, which bears some similarity to the uncomplexed species.

The 77 K phosphorescence lifetimes $\tau_p$ for the complexes are reported
in Table 1. The lifetime for py–BBr₃ in *n*-butyl alcohol is decreased by 80%
relative to pyridine–H⁺ (py–H⁺). This decrease can be ascribed to a heavy

TABLE 1

Phosphorescence lifetimes of azines and complexes

| Compound | Phosphorescence lifetime $\tau_p$ (s) |
|----------|------------------------------------------|
| Py–H$^+$ | 3.5 [a] |
| Py–BBr$_3$ | 0.626 ± 0.05 |
| Isoquinoline | 0.900 ± 0.06 |
| Iso–H$^+$ | 1.167 ± 0.07 |
| Iso–BBr$_3$ | 0.790 ± 0.07 |

[a]From ref. 2.

atom effect (HAE) on the pyridine phosphorescent triplet state arising from the three bromine atoms on boron. For isoquinoline, the lifetime of the BBr$_3$ complex has decreased by only 30% relative to the value for isoquin-oline–H$^+$ (iso–H$^+$), reflecting a more modest HAE. As is indicated in the discussion below, the relative sizes of the HAEs and the observed changes in zero-field parameters for these complexes can be correlated within the same theoretical framework.

Figure 3 shows a typical ODMR spectrum obtained for the complexes. The ZFS parameters are listed in Table 2, together with the results from Motten and Kwiram [2] for comparison. The value of $D$ decreases from 0.134 cm$^{-1}$ for py–H$^+$ to 0.118 cm$^{-1}$ for py–BBr$_3$. For the isoquinoline
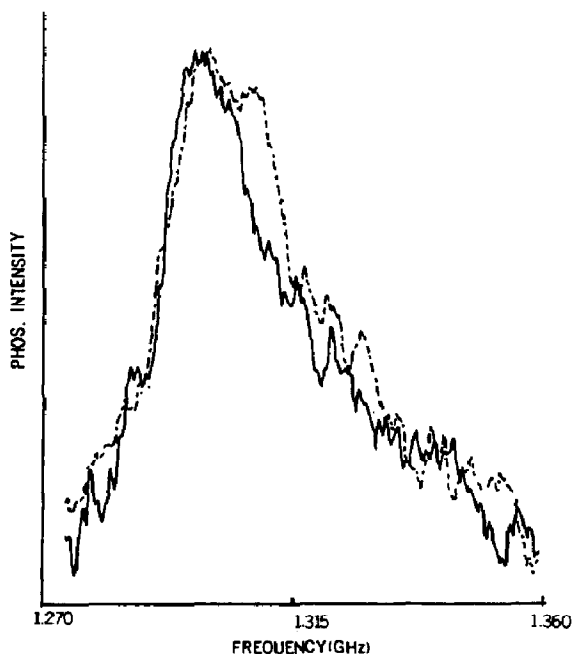


Fig. 3. ODMR spectrum of the $2|E|$ transition of py–BBr$_3$: ———, microwave sweep from low to high frequency; — — —, microwave sweep from high to low frequency.

**TABLE 2**

Zero-field splitting parameters of azines and complexes

| Compound | $D$ (cm$^{-1}$) | $|E|$ (cm$^{-1}$) |
|---|---|---|
| Pyridine | 0.165 [a] | 0.020 [a] |
| Py–H$^+$ | 0.134 [b] | 0.030 [b] |
| Py–BBr$_3$ | 0.118 ± 0.003 | 0.022 ± 0.001 |
| Isoquinoline | 0.100 [c] | 0.011 [c] |
| Iso–H$^+$ | 0.112 ± 0.005 | 0.016 ± 0.001 |
| Iso–BBr$_3$ | 0.115 ± 0.005 | 0.015 ± 0.005 |

[a]Predicted by calculations (see ref. 5).
[b]In ethylene glycol glass (see ref. 2).
[c]In durene (see ref. 10).

complexes, $D$ and $|E|$ are the same for iso–H$^+$ and isoquinoline–BBr$_3$ (iso–BBr$_3$) within experimental error.

One proposed explanation for the decrease in $D$ on protonation of azines is that the mixing of $^3n$–$\pi^*$ and $^3\pi$–$\pi^*$ states is enhanced by a geometric distortion of the planar aromatic framework on complexation [3]. Since $^3n$–$\pi^*$ states have large negative $D$ values [11] the admixture of such a state into a $^3\pi$–$\pi^*$ state which has a positive $D$ would cause a decrease in $D$ [12] for the phosphorescent state. However, this explanation seems to be rather unlikely because of the substantial increase in the energy of the $^3n$–$\pi^*$ state which results from complexation. For example, in aminopyridine, protonation is believed to increase the energy of the lowest $^3n$–$\pi^*$ state by about 20 000 cm$^{-1}$ [13]. Since the degree of vibronic mixing between two states depends on the energy gap between those two states [14], the mixing is expected to be unimportant for the complexed species, even in a favorable geometry.

We propose that these effects may be described in terms of a substituent model, such as has been proposed for various benzene derivatives [6]. Specifically, it appears that the BBr$_3$ acts like a substituent on pyridine, exerting both an inductive effect from the electronegative BBr$_3$ and a mesomeric effect introducing charge transfer configurations into the pyridine triplet wavefunction. Such contributions are known to reduce $D$ and $|E|$ [6, 15] and could potentiate the HAE by facilitating the delocalization of spin onto the heavy atom center.

The increase in $D$ for isoquinoline on protonation was somewhat unexpected and is not consistent with the general trend for azines. At present the mechanism for this increase is not obvious but we note that the increase is significantly smaller than the corresponding decrease for pyridine on protonation and suggest that the change for isoquinoline could reflect the effect of different chemical environments in the crystal lattices.

Comparing the two isoquinoline complexes, we see no change in $D$ going from protonation to the BBr$_3$ complex. This would be consistent

with observations on naphthalene, an analogous double-ring system. It would be expected that expansion of the $\pi$ system would favor delocalization of the unpaired electrons. Thus groups which slightly extend the conjugation will be less effective in reducing the $D$ parameter via mesomeric effects [16] relative to what would be expected in smaller $\pi$ systems. The changes in $D$ for extended $\pi$ systems such as naphthalene due to inductive effects are also not large relative to the benzene system. Apparently, the inductive reduction in symmetry for such systems introduces only very small amounts of configurational mixing [6]. For example the $D$ ($cm^{-1}$) values in the series naphthalene (0.1008), quinoline (0.1030), isoquinoline (0.1004) and quinoxaline (0.1007) do not vary by much despite the perturbation of introducing the more electronegative nitrogen into the ring [6]. By contrast, calculations of mesomeric and inductive effects on the ZFS parameters of benzene, a $\pi$ system analogous to pyridine, show that these effects should be more pronounced for benzene than for naphthalene; indeed the substituent effects on the ZFS parameters of benzene are much larger experimentally [6].

Returning to the isoquinoline complexes, we note that the rather modest HAE observed for iso–$BBr_3$ suggests that there is little charge transfer character in the triplet state of the iso–$BBr_3$ complex. Thus the phosphorescent states of the protonated and $BBr_3$ complexes appear to be very similar.

The use of substituent effects to describe Lewis acid complexes of azines has not, to our knowledge, been proposed previously. By choice of Lewis acids with well-characterized mesomeric and inductive effects, the general applicability of such a description could be tested.

## Acknowledgments

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