

Short Communication

Phosphorescence from pyridine induced by molecular complexation

R. SNYDER and A. C. TESTA

Department of Chemistry, St. John's University, Jamaica, N.Y. 11439 (U.S.A.)

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The absence of luminescence from pyridine in condensed media has remained a perennial problem of interest to many photochemists. Observation of the very weak fluorescence from pyridine vapor ($\phi_f \approx 10^{-4}$) was recently reported [1]. In contrast benzene exhibits fluorescence and phosphorescence [2]. It is generally accepted that the lowest triplet state in pyridine is π, π^* and, despite the contrary, phosphorescence should be expected. The explanation for the lack of luminescence may involve efficient internal conversion, $S_1 \rightsquigarrow S_0$, or a low triplet yield, a reversible non-productive photochemical event, or efficient radiationless decay in the triplet state, $T_1 \rightsquigarrow S_0$. From fluorescence lifetime and flash photolysis studies with some aminopyridines we have previously provided evidence that the triplet yield is solvent dependent [3, 4]. The triplet yield of pyridine has been determined to be 0.03 [5, 6]. If indeed there are triplets formed in the excitation of pyridine then in principle some perturbation technique such as protonation or complexation may enhance the possibility of observing luminescence. A successful attempt at the former has recently been realized [7]. The present study deals specifically with phosphorescence induced by complexation.

Upon addition of a Lewis acid such as BCl_3 to pyridine in cyclohexane a 1:1 complex is generated whose formation has been known for some time [8]. Complexation of the pyridine leads to changes in its UV absorption spectrum, which are shown in Fig. 1. The appearance of a new absorption band with a maximum at 265 nm is attributed to the electron donor-acceptor (EDA) complex.

Irradiation with 254 nm of 1.4×10^{-4} M pyridine with 3.5×10^{-5} M BCl_3 in cyclohexane at 77 K gives rise to an unstructured phosphorescence with a peak at 429 nm which is shown in Fig. 2. Since neither pyridine nor BCl_3 luminesce this emission can readily be attributed to the lowest triplet state of the EDA complex, whose energy is below that of the pyridine triplet (3.69 eV) [9]. The phosphorescence intensity increases with BCl_3 concentration; however, precipitation of the solid EDA complex occurred when $[\text{BCl}_3]$ exceeded 4×10^{-5} M, which limited the concentration range studied.

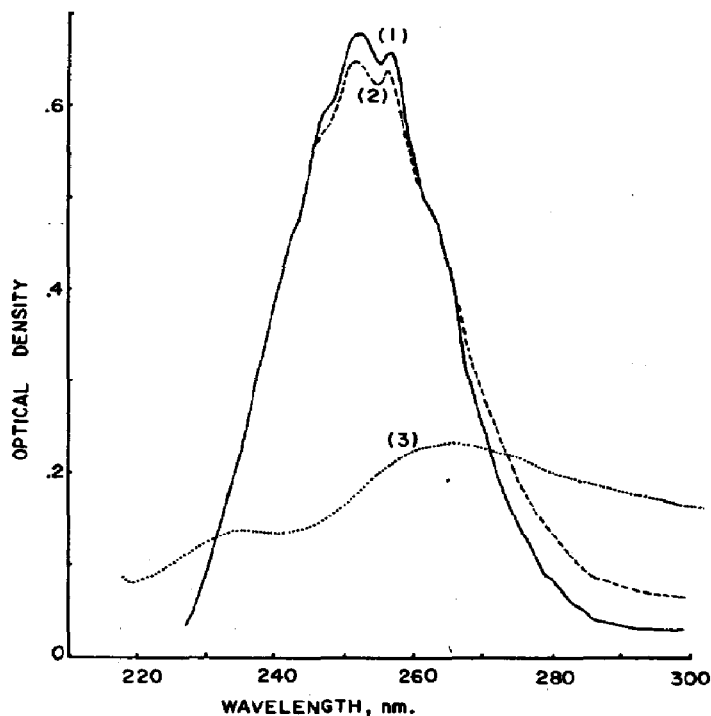


Fig. 1. UV absorption changes of 3.3×10^{-4} M pyridine in cyclohexane upon addition of BCl_3 : (1) no BCl_3 , (2) 1.1×10^{-5} M BCl_3 . Spectrum (3) is that of 6.6×10^{-5} M pyridine with 1.4×10^{-4} M BCl_3 , which shows a new absorption band at 265 nm due to the complex.

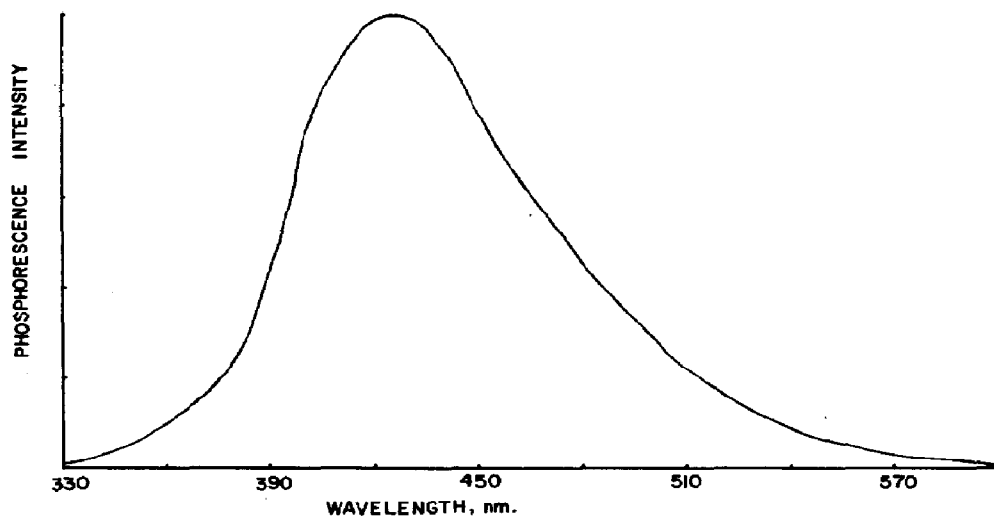


Fig. 2. Phosphorescence emission from 1.4×10^{-4} M pyridine and 3.5×10^{-5} M BCl_3 in cyclohexane (77 K, 254 nm excitation).

It appears that the complexation involving the non-bonding electron pair on nitrogen has either increased intersystem crossing or removed an important radiationless process. The energy of the B-N bond formed in the complex is considerably greater than that of a hydrogen bond (5 - 8 kcal mol⁻¹) as is readily seen in the exothermicity of the reaction between pyridine and BCl₃ which is about 39 kcal mol⁻¹ [10, 11].

The energy of the charge transfer triplet state is 2.89 eV, using the emission maximum. The oxidation potential of the donor pyridine is reported to be +2.07 V against the saturated calomel electrode in acetonitrile [12]. In contrast the ability to reduce BCl₃ is not known on a quantitative scale. If we apply the equation $E_{CT} = E_{ox}(D/D^+) - E_{red}(A/A^-) + 0.32 \text{ V}$ [13], then we can calculate the one-electron reduction potential of BCl₃ to be approximately -0.50 V against the saturated calomel electrode.

Regarding the lack of phosphorescence from pyridine it appears that the influence of the non-bonding electron pair in enhancing radiationless processes in the singlet and triplet states has been sufficiently minimized by complexation to allow phosphorescence.

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