

Excited-state Intramolecular Proton Transfer (ESIPT)-type Phosphorescence of 2-Aminobenzophenone in 77 K Matrices

Masahide Hagiri, Nobuyuki Ichinose,* Jun-ichiro Kinugasa, Tatsuya Iwasa, and Toshihiro Nakayama*
*Department of Chemistry and Materials Technology, Faculty of Engineering and Design, Kyoto Institute of Technology,
Matsugasaki Gosho-Kaidocho, Sakyo-ku, Kyoto 606-8585*

(Received December 5, 2003; CL-031190)

Time-resolved luminescence study of 2-aminobenzophenone in rigid matrices at 77 K has revealed its fluorescence and phosphorescence. The Phosphorescence consisted of two components with different bond structures, triplet energies, lifetimes, and anisotropies. These behaviors were explained by the presence of two ground-state conformers of 2-ABP with different reactivities for the excited-state intramolecular proton transfer.

The excited-state intramolecular proton-transfer (ESIPT) reactions have recently attracted much interests from theoretical, spectroscopic, and practical viewpoints because this serves simple and ultrafast examples of intramolecular reactions leading to efficient dissipation of photon energy without any chemical changes in the molecule or surrounding media.¹ As a practical application of ESIPT-active molecules, 2-hydroxybenzophenone, 4-hydroxybenzotriazole, and their related compounds are often used as polymer photostabilizer. ESIPT in carbonyl compounds with hydrogen-chelate structures efficiently leads to fluorescence emission from excited tautomer (enol form). Although there have been a number of fluorescence studies on ESIPT-active molecules especially by femtosecond time-resolved fluorescence spectroscopy, fewer studies on their phosphorescence from triplet enols.² This letter describes the observation of weak phosphorescence from photoenol of 2-aminobenzophenone (2-ABP).

The $S_1 \leftarrow S_0$ absorption band of 2-ABP in ethanol exhibited a peak at 379 nm with an extinction coefficient of $5.5 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The peak position shifted to the blue down to 370 nm (in cyclohexane) with the decrease of the solvent polarity.³ These results suggested that the transition has a π, π^* character. Time-resolved luminescence spectroscopy of 2-ABP in EPA matrix at 77 K has revealed its fluorescence and phosphorescence emission as indicated in Figure 1.^{3,4} It was essential to use an image-intensified gated multichannel spectrometer for the detection of the phosphorescence because of extremely high contrast in intensity of the strong short-lived fluorescence and the weak long-lived phosphorescence.⁵ The fluorescence spectrum was observed around 470 nm immediately after excitation. The phosphorescence spectrum was anomalously broad and was ranging from 370 to 650 nm. The fluorescence spectrum appears at longer wavelength than the origin of the phosphorescence spectrum. This means that the fluorescence is due to different species from the excited singlet state of parent 2-ABP. The shorter wavelength part (<490 nm) of the phosphorescence showing vibrational structure was analogous to those of benzophenones.⁸ For this reason, this component can be assigned to the emission from the excited triplet state of 2-ABP. We ob-

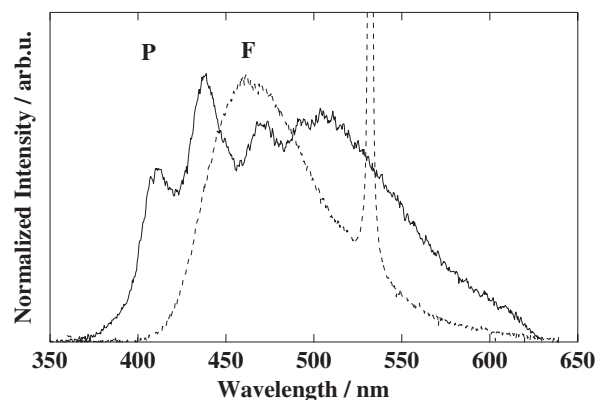


Figure 1. Fluorescence (dashed line) and phosphorescence (solid line) spectra of 2-ABP in EPA matrix at 77 K, measured at immediately after the laser excitation (gate time 30 ns) and at after the decay of the fluorescence (delay 100 ns, gate time 1 ms).

served a transient absorption of the excited triplet state of 2-ABP in 77 K EPA matrix, which was similar to that observed by electron-pulse radiolysis in benzene.⁹ The structureless band of the phosphorescence appeared in a longer wavelength region than that where the fluorescence appeared. Phosphorescence anisotropy measurement has indicated an anisotropy value of -0.12 for the phosphorescence around 400 nm, and 0.2 for the latter broad band. This strongly suggests that the two phosphorescence bands originate in different species.

Carbonyl oxygen can form intramolecular hydrogen bonding with hydroxy or amino group when formation of 5- or 6-membered ring is favored. This is the case for 2-ABP as the intramolecular hydrogen bonding ($\text{H}-\text{N}-\text{H}\cdots\text{O}=\text{C}$) has been indicated by IR spectroscopy.¹⁰ This could be also favorable for faster ESIPT than intersystem crossing. Since similar photophysical behavior has also been observed in the 77 K methylcyclohexane/2-methylbutane (MCH/IP) matrix, it would be reasonable to assign the fluorescence to the excited singlet of the enol form as a product of ESIPT of 2-ABP. We have assigned the phosphorescence to the excited triplet state of the enol to explain its spectral similarity to the fluorescence.¹¹ An external heavy atom effect on the fluorescence and phosphorescence also supported the assignment. The addition of ethyl iodide (0.5 M) in the EPA matrix quenched the fluorescence by 5%, whereas the broad phosphorescence intensity was increased by 15% indicating the enhancement of intersystem crossing and phosphorescent transition (Figure 2). However, intensity of the benzophenone-type phosphorescence was not affected by the addition of ethyl iodide possibly owing to the fast intersystem crossing from the

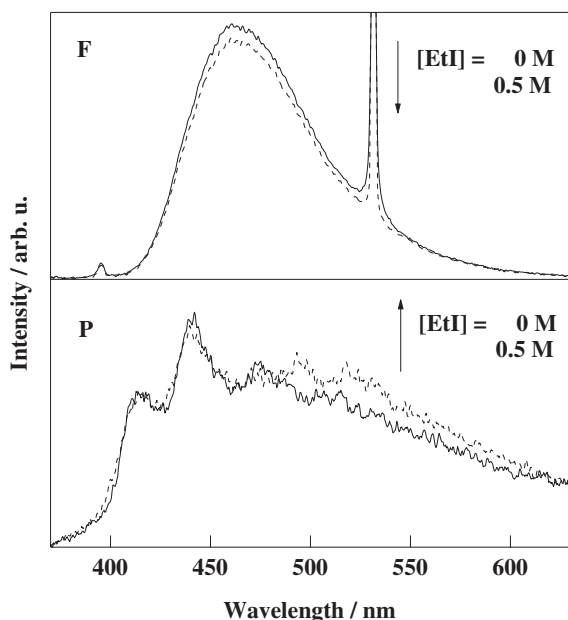
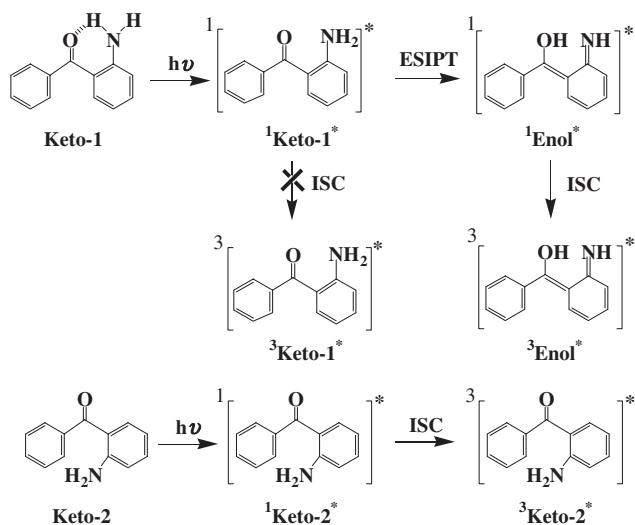


Figure 2. External heavy-atom effect of ethyl iodide (EtI) on the fluorescence and phosphorescence of 2-ABP in 77 K EPA matrix.

S_1 state.

Generally, ESIPT proceeds much faster than intersystem crossing to give excited enol adiabatically. However, fluorescence of 2-ABP was not observed in solution at room temperature. This could be due to fast back proton transfer as a quenching process. Even at 77 K fluorescence lifetime was too short to determine but was estimated to be <2 ns. Since phosphorescence from the triplet keto form was observed, ESIPT quantum yield should be less than unity. These behaviors are attributable to



Scheme 1.

the presence of two conformers concerning to the carbonyl-2-aminophenyl bond of 2-ABP in the 77 K matrices. Two phosphorescence bands decayed independently, suggesting that ESIPT via triplet state is not important. The broad phosphorescence had a lifetime of ≈ 7 ms (600 nm) which is shorter than that of the structured one (12–14 ms) observed at 410 nm. In other words, excited singlet state of hydrogen-bonded isomer undergoes ESIPT and the other will not react or react slowly and this also could be true for the excited triplet states of the conformers.

In summary, luminescence of 2-ABP in rigid matrices has exhibited photophysical behaviors of both keto- and enol-isomers owing to the presence of two ground-state conformers with different ESIPT reactivities (Scheme 1).

References and Notes

- 1 S. Ameer-Beg, S. M. Ormson, R. G. Brown, P. Matousek, M. Towrie, E. T. J. Nibbering, P. Foggi, and F. V. R. Neuwahl, *J. Phys. Chem. A*, **105**, 3709 (2001) and references cited therein.
- 2 P.-T. Chou, C.-S. Chiou, W.-S. Yu, G.-R. Wu, and T.-H. Wei, *Chem. Phys. Lett.*, **370**, 747 (2003).
- 3 Glass forming solvents; EPA is a mixture of diethyl ether:2-methylbutane:ethanol = 5:5:2 (v/v), and MCH/IP is also a mixture of methylcyclohexane:2-methylbutane (isopentane) = 1:4 (v/v). Absorption spectrum of 2-ABP in EPA matrix shifted to red by 10 nm. The fluorescence excitation spectrum was almost the same as the absorption spectrum.
- 4 Third harmonic pulses (355 nm, 6 ns, 30 mJ pulse⁻¹) of a Nd:YAG laser (Continuum Surelite I-10) and a gated image-intensified multichannel spectrometer (UNISOKU TSP-501) were used for the fluorescence and phosphorescence measurements. A Xe flash was used as a monitor light for the transient absorption measurement.
- 5 Apparent fluorescence and total phosphorescence quantum yields of 2-ABP in EPA matrix at 77 K were estimated to be 0.06 ± 0.01 and $9 \pm 2 \times 10^{-6}$, respectively, by measuring the relative emission intensities to those of 9-fluorenone.^{6,7} Phosphorescence excitation spectra of 2-ABP could not be obtained by our spectrofluorometer.
- 6 C. Huggenberger and H. Labhart, *Helv. Chim. Acta*, **61**, 250 (1978).
- 7 T. F. Hunter, *Trans. Faraday Soc.*, **66**, 300 (1970).
- 8 N. J. Turro, in "Modern Molecular Photochemistry," Benjamin, Menlo Park (1978), Chap. 5, p 116.
- 9 A. K. Singh, D. K. Palit, and T. Mukherjee, *J. Phys. Chem.*, **106**, 6084 (2002).
- 10 L. J. Bellamy and R. J. Pace, *Spectrochim. Acta, Part A*, **28**, 1869 (1972).
- 11 The vibrational spacing in the benzophenone-like phosphorescence was ≈ 1500 cm⁻¹, which was smaller than those for the typical C=O stretching observed in the n, π^* phosphorescence of aromatic ketones (≈ 1700 cm⁻¹).^{5,8} This suggests that the electronic character of the phosphorescence state is π, π^* .
- 12 J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).