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  - (12) The mixture of **2d** and **2e** was unavoidably produced in the cycloaddition (Table I). Moreover, **2d** and **2e** will isomerize each other prior to the rearrangement. Therefore, the experiments described hereafter were carried out with a mixture of **2d** and **2e** (4:1 ratio unless otherwise cited), designated as **2d,e**.
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- Since **1d** should produce a larger amount of **3** than **1c**, the results are not compatible with the cycloreversion-recombination as well. The ease of the rearrangement of **2c** relative to **2d,e** will be the reason for the difference.
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## The Ultraviolet Transitions of Benzoic Acid. 3. Effects of Hydrogen Bonding on the Emission Properties

J. Clayton Baum\*

Contribution from the Frick Chemical Laboratory, Princeton University,  
Princeton, New Jersey 08540. Received June 19, 1978

**Abstract:** Contrary to previously published results, the energies and quantum yields of the fluorescence and phosphorescence of benzoic acid in isopentane-methylcyclohexane at 77 K are found to be independent of the excitation wavelength in the 280-nm region. Further, the excitation spectra monitoring the fluorescence and phosphorescence are identical. These data are consistent with the fact that benzoic acid exists only as dimers in pure hydrocarbon glasses. Irradiation of methylcyclohexane gives photoproducts which hydrogen bond to benzoic acid. The absorption, emission, and excitation spectra of this latter solution of benzoic acid do agree with those previously reported. The earlier hypothesis that there is a  $^3n\pi^*$  state close in energy to the  $^1L_b$  state of benzoic acid remains valid, however. The role (acceptor or donor) of benzoic acid in hydrogen bonding and the effect of hydrogen bonding on the energies of both  $\pi\pi^*$  and  $n\pi^*$  states are considered in examining the emission properties of the molecule.

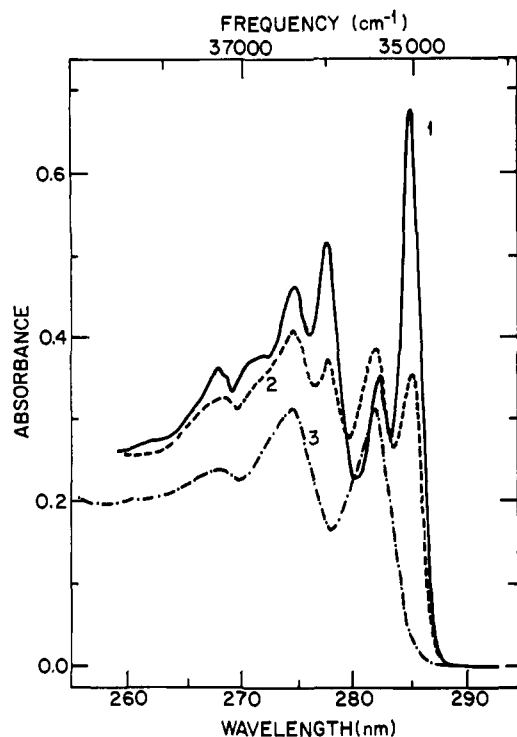
### I. Introduction

There have been many studies describing the phosphorescence of benzoic acid but until recently no fluorescence was observed. Baba and Kitamura<sup>1</sup> were the first to report both types of emission from benzoic acid. They found that in an isopentane-methylcyclohexane (IP-MCH) glass (6:1 by volume) the fluorescence/phosphorescence intensity ratio of benzoic acid was much greater for 285-nm excitation than for excitation at 281 nm. The excitation spectra obtained by monitoring the fluorescence (310 nm) and phosphorescence (410 nm) were also quite different. The authors explained their

results in terms of the molecular association of benzoic acid. They concluded that, while the dimer species can both fluoresce and phosphoresce, the monomer only phosphoresces.

It is well known that the emission properties of heteroatomic molecules are dependent upon the relative energies of the  $\pi\pi^*$  and  $n\pi^*$  singlet and triplet states.<sup>2</sup> Baba and Kitamura<sup>1</sup> offered the following mechanism to rationalize the emission behavior of benzoic acid in the hydrocarbon glass. They assumed that a  $^3n\pi^*$  state lies slightly below the lowest  $^1\pi\pi^*$  state and above the lowest  $^3\pi\pi^*$  state in the monomer species. This leads to efficient intersystem crossing and only phosphorescence would be expected. The authors hypothesized that hydrogen bonding in the dimer raises the  $^3n\pi^*$  state above the  $^1\pi\pi^*$  state, decreasing the amount of intersystem crossing.

\* Please address correspondence to the author at Department of Chemistry, Florida Institute of Technology, Melbourne, Fla. 32901.



**Figure 1.** Effect of photolysis (450-W high-pressure mercury lamp) on the  ${}^1L_b$  absorption of  $2.1 \times 10^{-4}$  M benzoic acid in IP-MCH (6:1). Irradiation time: (1) 0; (2) 9; (3) 39 h. Path length of sample tube is 13 mm.

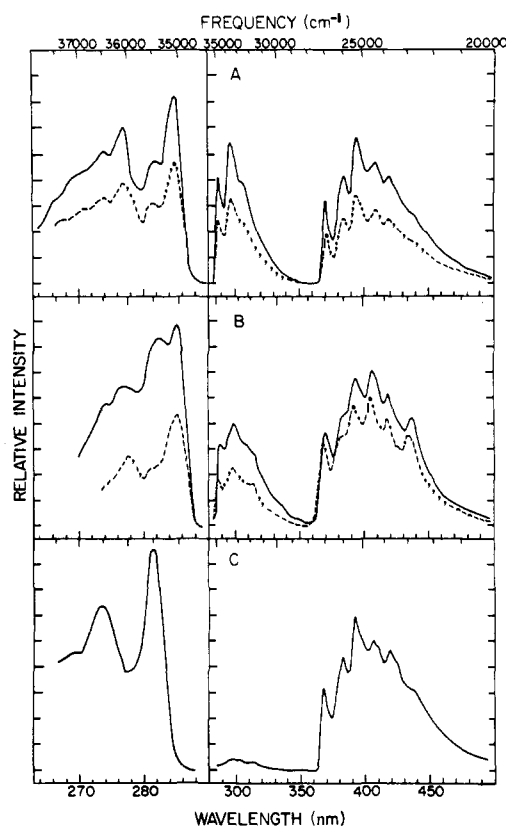
This would allow both fluorescence and phosphorescence to occur.

The experiments of Baba and Kitamura<sup>1</sup> were based on the interpretation<sup>3</sup> that the absorption peaks in the 280-nm band of benzoic acid are due to the presence of both monomer and dimer species in the hydrocarbon glass. We have shown, however, that only the dimer of benzoic acid exists at 77 K in non-hydrogen-bonding solvents.<sup>4</sup> To resolve this apparent discrepancy we decided to repeat the work of Baba and Kitamura. The emission properties of benzoic acid are considered in light of our new results and the influences of hydrogen bonding are discussed. Detailed analyses of the fluorescence and phosphorescence line spectra of benzoic acid at 4.2 K will be given in later papers.<sup>5,6</sup>

## II. Experimental Section

**Measurement of the Electronic Spectra.** The ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. The emission excitation source was a General Electric Model AH-6 (1000 W) high-pressure mercury lamp whose output was passed through a 0.25-m Bausch and Lomb monochromator; the emission was observed at right angles to the excitation through a 0.50-m Bausch and Lomb monochromator. Both gratings were blazed for 300 nm. An RCA 1P28 phototube was located at the exit of the analyzing monochromator. The phototube signal was fed into a Jarrell-Ash electrometer amplifier whose output was recorded by a Moseley Model 7101 BM strip-chart recorder.

The emission curves were recorded automatically. The excitation plots were made point by point at nanometer intervals by manually changing the excitation wave length. The emission spectra were corrected for the wavelength dependence of the grating efficiency and phototube response. A trace of the lamp output measured as a function of wavelength with the calibrated monochromator and phototube was used to correct the excitation spectra. The wavelength readings were calibrated using standard mercury lines. The typical band-passes for the emission spectra were 1.8 nm for the excitation monochromator and 2.4 nm for the analyzing monochromator. For the excitation spectra the band-passes were 0.9 and 6.0 nm for the exciting and analyzing monochromators, respectively. The samples were studied at



**Figure 2.** Excitation (left) and emission (right) spectra of  $2.1 \times 10^{-4}$  M benzoic acid in IP-MCH (6:1) at 77 K taken after (A) 0 h; (B) 9 h; (C) 39 h of irradiation with a 450-W high-pressure mercury arc. Excitation spectra were obtained by monitoring the phosphorescence (410 nm) (—) and the fluorescence (310 nm) (---). Emission spectra were obtained by excitation at 285 (—) and 281 nm (---).

77 K by inserting them into a quartz Dewar which has three Suprasil windows located at 90° intervals.

**Preparation of Samples.** Zone-refined (99.9+%) benzoic acid was purchased from the Aldrich Chemical Co. "Spectroquality" isopentane (IP) and methylcyclohexane (MCH) were obtained from Matheson Coleman and Bell and stored over  $P_2O_5$ . The solvents were generally mixed in the 6:1 (IP:MCH) ratio used by Baba and Kitamura. After the solutions were prepared they were degassed by freezing, evacuation, and thawing until the trapped-gas pressure was below  $1 \times 10^{-6}$  Torr.

## III. Presentation and Interpretation of Results

**Absorption Spectra.** The absorption spectrum of a  $2.1 \times 10^{-4}$  M solution of benzoic acid in IP-MCH (6:1) at 77 K is shown in Figure 1 (spectrum 1). The frequencies and relative intensities of the peaks are the same as for benzoic acid in other hydrocarbon solvents.<sup>7</sup> These values also agree with the 90 K spectrum published by Ito et al.<sup>3</sup> As we showed in part 1, this spectrum belongs to benzoic acid dimers.<sup>4</sup> The absorption spectra of degassed solutions of benzoic acid in IP-MCH after 9 and 39 h of irradiation at room temperature with a 450-W mercury lamp are also presented in Figure 1 (spectra 2 and 3, respectively). It is important to note that spectrum 2 is quite similar to the absorption spectrum published by Baba and Kitamura.<sup>1</sup> In this case the integrated intensity of the absorption has decreased and the second, fourth, and sixth peaks have increased in intensity relative to the other peaks. In spectrum 3 the absorption by the dimer of benzoic acid has disappeared.

**Emission and Excitation Spectra.** The 77 K excitation and emission spectra of degassed solutions of benzoic acid in IP-MCH after different periods of irradiation at room temperature are presented in Figure 2. Spectra taken at 77 K rather

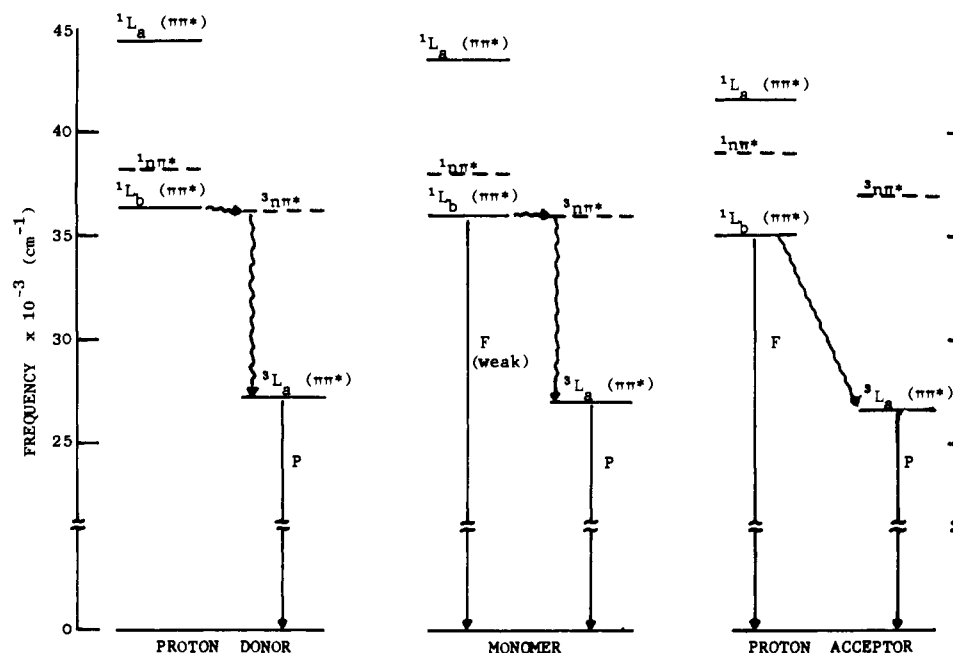


Figure 3. Energy level diagrams for benzoic acid as a proton donor, monomer, and proton acceptor.

Table I. Assignment of the Fluorescence and Phosphorescence Peaks of Benzoic Acid in Isopentane-Methylcyclohexane at 77 K

$\lambda$ , nm	$\nu$ , $\text{cm}^{-1}$	$\Delta\nu$ , $\text{cm}^{-1}$	assignment
Fluorescence			
$287 \pm 0.5$	$34\,830 \pm 60$	0	origin
290 (shoulder)	34 470	360	$\nu_{6a}$
296	33 770	1060	$\nu_{12}$
305	32 780	2050	$2 \times \nu_{12}$
Phosphorescence			
$371 \pm 0.5$	$26\,950 \pm 30$	0	origin
385	25 970	980	$\nu_{12}$
394	25 370	1580	$\nu_{8a}$
410	24 380	2570	$\nu_{12} + \nu_{8a}$
420	23 800	3150	$2 \times \nu_{8a}$
438	22 830	4120	$2 \times \nu_{8a} + \nu_{12}$

than room temperature are presented because of the increased detail observable in them, and to shift all the H-bonding equilibria to completion. The wavelengths and relative intensities of the fluorescence and phosphorescence of the unphotolyzed sample are independent of the excitation wavelength (Figure 2A). Further, the excitation spectra monitoring the fluorescence (310 nm) and the phosphorescence (410 nm) are identical. These results are consistent with the fact that benzoic acid exists only as dimers in pure hydrocarbon solvents at 77 K.<sup>8</sup> (The emission and excitation curves were unchanged when MCH that had been treated with sulfuric acid, distilled, and dried over cesium<sup>9</sup> was used.) The vibrational assignments for the fluorescence and phosphorescence peaks are given in Table I.

After 9 h of irradiation at room temperature, the emission and excitation spectra of benzoic acid samples became similar to those published by Baba and Kitamura<sup>1</sup> (Figure 2B). When the excitation wavelength is changed from 285 (solid curve) to 281 nm (dashed curve), the fluorescence/phosphorescence ratio decreases and the spectra shift to the blue. The phosphorescence and fluorescence excitation spectra also differ, indicating two emitting species. The intensity increase in the 282-nm peak of the phosphorescence excitation curve reflects the enhancement of that peak in the absorption spectrum (Figure 1, spectrum 2) upon photolysis.

The emission and excitation spectra of benzoic acid in IP-MCH after 39 h of irradiation are shown in Figure 2C. There is very little fluorescence, and the phosphorescence excitation spectrum coincides with the new absorption spectrum. The phosphorescence origin is now  $180 \text{ cm}^{-1}$  higher in energy than the origin of the dimer phosphorescence. Evidently there has been nearly complete conversion of the benzoic acid dimer to some other benzoic acid species.

**Quantum Yields.** The relative quantum yields of fluorescence and phosphorescence were found by replotting the emission intensities as linear functions of the frequency. This gives a fluorescence/phosphorescence ratio of 0.79 for benzoic acid in IP-MCH. Using the published value<sup>1</sup> for the quantum yield of total emission (0.70), the quantum yields of phosphorescence and fluorescence are 0.39 and 0.31, respectively. It is interesting that the quantum yields of phosphorescence (0.44) and fluorescence (0.26) that we obtained by the same procedure for the benzoic acid sample irradiated for 9 h are the same as the quantum yields reported by Baba and Kitamura for the dimer.

**Photochemistry.** The photochemical change was a permanent one, created and maintained at room temperature. Although we have found that benzoic acid dimer can undergo photolysis even at low temperature,<sup>7</sup> the principal spectral changes in this study could be reproduced by adding unphotolyzed benzoic acid to a solution of IP-MCH containing MCH that had been irradiated. Thus, there must be photoproducts of MCH that interact with benzoic acid to give the absorption and emission changes. The absorption and emission spectra of benzoic acid in the photolyzed MCH are very similar to the spectra of the acid in other solvents containing molecules that can hydrogen bond to it.<sup>7,10</sup> This strongly suggests the photolytic formation of such species in MCH.

We irradiated "spectroquality" MCH without removal of dissolved air with an unfiltered Hanovia 450-W high-pressure mercury lamp for 64 h at room temperature. New ultraviolet absorption appeared in the MCH at 330 nm with a maximum at 275 nm. Infrared, NMR, and mass spectrum analyses of the irradiated solvent led to the conclusion<sup>7</sup> that two of the photoproducts are isomers of methylcyclohexanone and methylcyclohexanol—both capable of hydrogen bonding with benzoic acid. While this sample of MCH was irradiated in the presence

of air, sealed, degassed samples of benzoic acid in MCH also showed new carbonyl and hydroxyl IR peaks after irradiation at room temperature. There are two possible explanations for the presence of oxygen in the latter samples. First, it is conceivable that even after extensive degassing dissolved oxygen remains in solution. Second, the benzoic acid may itself be the source of oxygen.

It seems unlikely that Baba and Kitamura<sup>1</sup> could have photolyzed their samples during their emission studies. It is very possible, however, that the MCH they used "without further purification" contained initial impurities capable of hydrogen bonding with benzoic acid.

#### IV. Discussion

We doubt the assertion of Baba and Kitamura<sup>1</sup> that the free monomer of benzoic acid was present in their study, but the model they proposed to explain the effect of dimerization on the emission properties of benzoic acid (which is outlined in the Introduction) remains essentially valid.

In aromatic carbonyl compounds (PhCOR), the resonance interaction of an electron-releasing R group having lone-pair electrons will destabilize the  $\pi^*$  orbital more than the  $n$  orbital causing a blue shift of the  $n\pi^*$  states.<sup>11</sup> This effect is illustrated by the reversal of the lowest singlet and triplet excited states from  $n\pi^*$  in benzaldehyde (R = H) to  $\pi\pi^*$  in benzoic acid (R = OH).<sup>4,12</sup> The energy level diagram for benzoic acid is shown in Figure 3. The energies of the  $^1\pi\pi^*$  states are those reported in part 1. High-resolution spectroscopic experiments on the effect of various crystalline solvents on the energy shifts and the fluorescence/phosphorescence ratio of methyl benzoate show that the  $^3n\pi^*$  state is about  $200\text{ cm}^{-1}$  below  $^1L_b$  in this molecule.<sup>5</sup> Since R = OH is more electron releasing than R = OCH<sub>3</sub>, the  $^3n\pi^*$  state in the monomer of benzoic acid is energetically higher than in methyl benzoate; from experiment<sup>4</sup> we know that the  $^1L_b$  state of the benzoic acid monomer is at lower energy ( $\sim 130\text{ cm}^{-1}$ ) than the same state in methyl benzoate. Therefore, the  $^1L_b$  and  $^3n\pi^*$  states are likely to be nearly degenerate in the monomer of benzoic acid and this is shown in the center of Figure 3.

In examining the influence of hydrogen bonding on the emission properties of benzoic acid two points must be kept in mind. First, the role of benzoic acid as proton donor and/or acceptor in hydrogen bonding is important. Second, hydrogen bonding will affect the energies of both  $n\pi^*$  and  $\pi\pi^*$  states. Hydrogen-bonded complexes of benzoic acid (BA) and methyl benzoate (MB) are divided below into two categories—complexes in which the aromatic partner acts principally as a proton donor or as a proton acceptor.

proton donor		ref
BA in EPA	no fluorescence	13
BA in ethanol	no fluorescence	14
proton acceptor		ref
BA in 1P-MCH (dimer)	fluorescence	this work
MB in 1P-MCH-acetic acid	fluorescence	1
MB in EPA	weak fluorescence	12

It is clear that the fluorescence of benzoic acid depends on its role in hydrogen bonding.

When benzoic acid is a proton donor, the  $\pi\pi^*$  states are increased in energy (Figure 3).<sup>10</sup> Hydrogen bonding by the hydroxyl group increases its electron-repelling ability and this

should increase the energy of the  $^3n\pi^*$  state. The lack of fluorescence from complexes in which benzoic acid acts most strongly as a proton donor indicates that the blue shift of the  $^3n\pi^*$  state is small enough ( $<300\text{ cm}^{-1}$ ) that this state is still located below but near  $^1L_b$  and efficient intersystem crossing occurs, as shown on the left in Figure 3.

The  $\pi\pi^*$  states of benzoic acid decrease in energy when the molecule acts as a proton acceptor in hydrogen bonding.<sup>10</sup> The nonbonding electrons on the carbonyl oxygen are involved in the hydrogen bond, and the  $^3n\pi^*$  state should increase in energy because the stabilization of the ground state by the hydrogen bond is greater than that of the excited state where the oxygen has lost nonbonding-electron density. In this situation the  $^3n\pi^*$  state becomes higher in energy than  $^1L_b$  as shown on the right in Figure 3, and the intersystem-crossing rate is lowered. This change allows benzoic acid to fluoresce strongly. The fluorescence of methyl benzoate is weaker in EPA (although stronger than the non-hydrogen-bonded species) than in acetic acid because the proton-acceptor bond in EPA is weaker. In other words, the  $^3n\pi^*$  blue shift and  $^1L_b$  red shift are smaller in EPA than in acetic acid. All the above results are consistent with the hypothesis that the  $^3n\pi^*$  and  $^1L_b$  lie close to each other.

#### V. Conclusion

The results of this study confirm the important hypothesis of Baba and Kitamura<sup>1</sup> that the intersystem-crossing process in benzoic acid is strongly dependent on the near degeneracy of an (unobserved)  $^3n\pi^*$  state with the  $^1L_b$  state. Further evidence for this model will be presented in a discussion of the high-resolution phosphorescence and fluorescence line spectra.<sup>5</sup> The role (acceptor or donor) of benzoic acid in hydrogen bonding and the effect of hydrogen bonding on the energies of both  $\pi\pi^*$  and  $n\pi^*$  states must be considered in examining the emission properties of the molecule. Contrary to the previously published data, our emission and excitation spectra are also consistent with the fact that benzoic acid exists only as dimers in pure hydrocarbon solvents at 77 K.

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