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  - BDHT**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.30 (m, 2H, *p*-phenyl), 6.93 (m, 4H, *m*-phenyl), 6.66 (d, 2H, thiophene), 6.42 (d, 2H, methylene), 3.05 (d, 2H, hydroxyl) EIMS:  $m/e$  368 ( $\text{M}^+$ ), 351 ( $\text{M-OH}^+$ ) Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{F}_4\text{O}_2$ : S: C, 58.71; H, 3.26. Found: C, 58.67; H, 3.24.
  - F<sub>8</sub>STPP**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 200 MHz):  $\delta$  9.84 (s, 2H, thiophene), 9.19 (s, 2H, pyrrole), 8.75 (q, 4H, pyrrole), 8.03 (m, 4H, *p*-phenyl), 7.59 (m, 8H, *m*-phenyl), -2.63 (s, 1H, NH) UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 422 (5.53), 506 (4.61), 612 (3.73), 666 (2.67) Anal. Calcd. for  $\text{C}_{44}\text{H}_{21}\text{F}_8\text{N}_3\text{S}$ : C, 68.14; H, 2.71; N, 5.42 Found: C, 68.19; H, 2.69; N, 5.40 **F<sub>8</sub>S<sub>2</sub>TTP**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  9.56 (s, 4H, thiophene), 7.37 (m, 8H, *m*-phenyl) UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 430 (5.28), 508 (4.68), 628 (3.09), 692 (3.81) Anal. Calcd. for  $\text{C}_{44}\text{H}_{20}\text{F}_8\text{N}_2\text{S}_2$ : C, 66.68; H, 2.52; N, 3.53 Found: C, 66.72; H, 2.49; N, 3.56.
  - Br<sub>3</sub>F<sub>8</sub>STPP**: UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 460 (5.01), 554 (4.01), 630 (3.53), 720 (3.42)  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ , 200 MHz):  $\delta$  7.94 (m, 4H, *p*-phenyl), 7.52 (m, 8H, *m*-phenyl) Anal. Calcd. for  $\text{Br}_3\text{C}_{44}\text{H}_{13}\text{F}_8\text{N}_3\text{S}$ : C, 37.56; H, 0.92; N, 2.99 Found: C, 38.01; H, 0.95; N, 2.91.
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  - Br<sub>4</sub>F<sub>8</sub>S<sub>2</sub>TTP**: UV-vis ( $\lambda_{\text{max}}$ , log $\epsilon$ ): 434 (5.24), 520 (4.44), 628 (3.66), 688 (3.61)  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  9.35 (s, 4H, thiophene), 7.34 (m, 12H, *m*, *p*-phenyl) Anal. Calcd. for  $\text{Br}_4\text{C}_{44}\text{H}_{16}\text{F}_8\text{N}_2\text{S}_2$ : C, 47.68; H, 1.44; N, 2.53 Found: C, 47.81; H, 1.40; N, 2.49.
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## Rovibronic Spectrum of Cold Benzyl Radical

Sang Kuk Lee

Department of Chemistry, College of Natural Sciences,  
Pusan National University,  
Pusan 609-735, Korea

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In high resolution electronic molecular spectroscopy, one of the most difficult works is to determine the structure of large molecules accurately, since large molecules have large principal moments of inertia  $I_A$ ,  $I_B$ , and  $I_C$  and consequently small rotational constants A, B, and C.<sup>1</sup> The typical values of the rotational constants are of the order of 0.1  $\text{cm}^{-1}$  in large molecules such as benzene derivatives. This means that the rotational energy levels are very closely spaced, leading to appreciable population of levels with  $J$  and  $K_a$  or  $K_c$  of the order of 100 at room temperature. As a result, something like 30,000 rotational transitions accompany any electronic or vibronic transition. The rotational transitions usually lie within *ca.* 30  $\text{cm}^{-1}$  so, on average, there is one transition for each 0.001  $\text{cm}^{-1}$ . Since the Doppler width of the transition in the gas phase is *ca.* 0.02  $\text{cm}^{-1}$  there may be about 20 transitions within the Doppler width. Thus, even with the highest resolution (*ca.* 0.02  $\text{cm}^{-1}$ ), there is little hope of resolving individual transitions.

What is observed is a rotational intensity contour with a characteristic shape. The shape of the contour strongly depends on the same parameters as one would obtain from a completely resolved spectrum, that is, the rotational selection rules (type A, B, and C or hybrid), the rotational temperature, and the rotational constants at both the ground and the excited electronic states. Also, it has been well known that the rotational contours are much more sensitive to the changes of rotational constants ( $\Delta A$ ,  $\Delta B$ , and  $\Delta C$ ) during the transition rather than to the absolute values of the constants.

The benzyl radical is a prototypical aromatic radical with seven delocalized  $\pi$  electrons and has been subjected to many spectroscopic studies. The first spectrum of benzyl radical was obtained in emission near 450 nm by Schüler *et al.*<sup>2</sup> A few years later, Porter and coworkers observed not only 450 nm band<sup>3</sup> but also 305 nm band<sup>4</sup> from the electronic absorption spectra employing the flash photolysis technique. Cossart-Magos and Leach<sup>5,6</sup> succeeded in determining the symmetry of the excited state at 450 nm from the analysis of rotational contour of the spectra. In addition, Cossart-Magos group has continued to analyze the rotational contours of the vibronic bands of the room temperature emission spectra of the methyl substituted benzyl radicals.<sup>7,8</sup> Recently, Carrick and Selco<sup>9</sup> have recently obtained a high resolution emission spectra of the benzyl radical. Also, laser induced fluorescence (LIF) method has been applied by many groups<sup>10-16</sup> to study the vibronic coupling of two lowest excited electronic states and to measure the lifetime of the benzyl radical.

As far as I am concerned, however, no one has so far succeeded in obtaining a reliable geometry data of the benzyl radical even in the ground state due to a limited resolution and a poor ratio of signal to noise of the spectra obtained.<sup>9</sup>

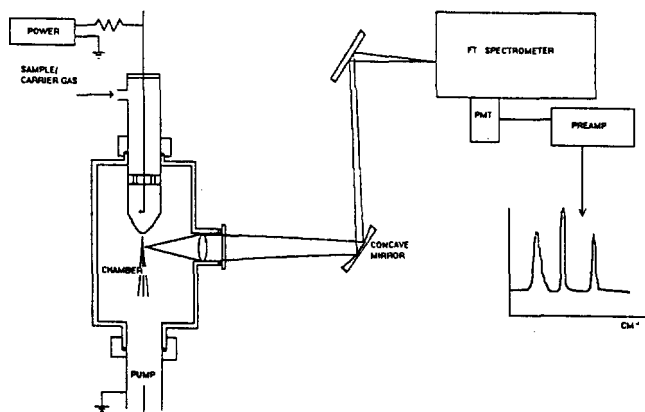


Figure 1. The experimental setup used in this experiment.

In this study, a high resolution emission spectra of the  $1^2A_2-1^2B_2$  electronic transition of the benzyl radical have been obtained using a high resolution Fourier transform visible spectrometer coupled with a technique of supersonic expansion.

The observation of high resolution emission spectra of benzyl radical in a jet has been performed using the experimental apparatus shown in Figure 1 which is very similar to those previously described.<sup>17,18</sup> For the generation of the benzyl radical, several possible precursors have been tested in terms of the maximum fluorescence and the stability of the discharge over a long period. Of the molecules tested in this experiment, the toluene exhibited the strongest intensity of fluorescence of the benzyl radical from the low resolution survey spectrum. Also, the discharge of the toluene has produced the minimum byproducts compared with benzyl halides. Thus, the toluene of the spectroscopic grade was purchased commercially from Aldrich and used without further purification. The vapors of the compound were expanded with an inert carrier gas He through the quartz nozzle into the vacuum chamber made by a six-way cross Pyrex glass tube of 5.0 cm in diameter. The concentration of the parent compound in a carrier gas could be controlled by immersing the sample in a temperature-controllable water bath. In this experiment, the concentration of the precursor was adjusted for the maximum fluorescence and believed to be about 1% in the gas mixture.

For the nozzle which is similar to one developed by Engeling,<sup>19</sup> a 10 mm inner diameter and 3 mm thick walled glass tube was flame heated until one end was narrowed to the desired size opening. For this experiment, the nozzle of about 0.2 mm in diameter of the orifice size has been used. The sharpened stainless steel anode of 2.0 mm in diameter and 30 cm in length was inserted inside the nozzle for an anode. The distance between anode electrode and the nozzle opening has been proven to be critical for the stability of the discharge over a long period. Thus, the stainless steel anode was firmly fixed into the center of the nozzle by means of the teflon holder.

The benzyl radical was formed in a jet by flowing the gas mixture over an electric *dc* discharge between the anode fixed inside the nozzle and the pump which acts as a cathode. The anode was connected to a 3000 volts *dc* power

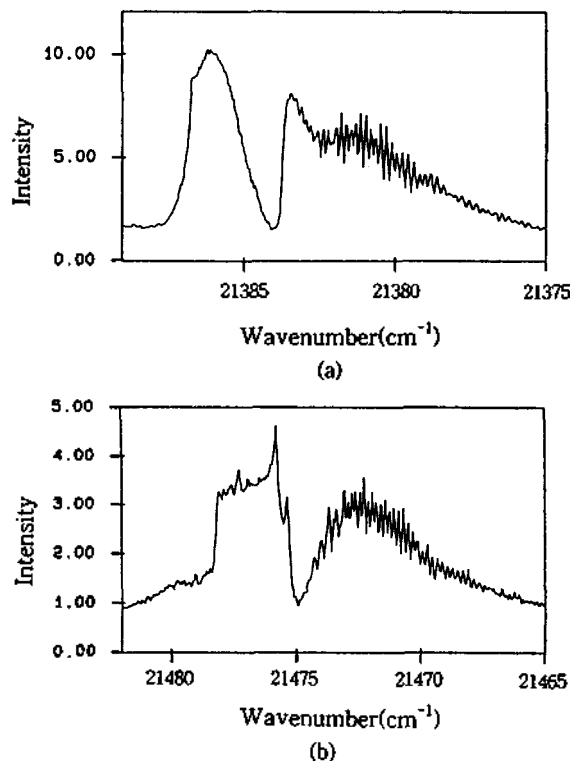


Figure 2. Low temperature rovibronic emission spectra of (a) the  $6a_1^0$  and (b) the  $6b_1^0$  vibronic bands of the  $1^2A_2-1^2B_2$  electronic transition of the benzyl radical located at 21384 and 21475  $\text{cm}^{-1}$ , respectively.

supply via a 500 K $\Omega$  current limiting ballast resistor. The typical operating condition was 4-6 mA discharge current at the 1000 volts potential. The backing pressure of the nozzle was measured to be about 2 atm. The pressure in the expansion chamber was maintained to lower than 1.0 Torr by using the mechanical vacuum pump. For increased collection of the fluorescence, a quartz lens ( $f=5.0$  cm,  $d=3.8$  cm) was placed near the nozzle inside the vacuum chamber. A jet area of 2 mm in diameter below the nozzle orifice was focussed onto the external port of the FT spectrometer (Bruker IFS-120HR).

The instrument was operated with a Quartz-vis beamsplitter, a home-made ac preamplifier and the PMT (Hamamatsu model 1P28) detector for photon counter. For the improvement of signal to noise ratio of the spectrum, a 10 nm band-pass of interference optical filter centered at 470 nm has been employed to block off strong fluorescence from the He gas, and the FT-spectrometer has been operated in manual mode rather than in automatic mode because the former one is supposed to be more useful for the weak emission spectra.<sup>20</sup> The output of the PMT detector was fed via an ac preamplifier to the computer for Fourier transform process. Initially, the survey scans were tried at 2.0  $\text{cm}^{-1}$  resolution over wide frequency range for optimizing the discharging condition. From the survey spectra obtained, it has been found that the two strongest peaks correspond to the  $6a_1^0$  and  $6b_1^0$  vibronic bands of the  $1^2A_2-1^2B_2$  electronic transition located at 21,384 and 21,475  $\text{cm}^{-1}$ , respectively. After the experimental conditions were optimized, higher resolution

scans were obtained at the resolution of  $0.05\text{ cm}^{-1}$  over the region from  $16,000$  to  $25,000\text{ cm}^{-1}$ . A total of 250 scans have been added together over 2 hrs. to obtain the final spectra shown in Figure 2. However, much longer integration times were not possible due to the deterioration of the discharge.

From the spectra obtained, the rotational fine structure is clearly seen in the P-branch region only. However, the R-branch peak does not show the rotational contours due to the limited cooling of benzyl radical compared to the resolution of the spectrometer. The ratio of signal to noise approaches about 100 in the spectra, which shows much improvement compared to about 7 of the previous report.<sup>9</sup>

In summary, the rotationally cooled benzyl radical has been generated in a jet by expansion with an inert buffer gas He from a high voltage electric *dc* discharge of the toluene. The high resolution spectra of the  $6a_1^0$  and  $6b_1^0$  vibronic bands of the  $1^2A_2-1^2B_2$  electronic transition of the benzyl radical have been obtained in emission using a high resolution Fourier transform visible spectrometer. From the comparison with the previous spectra reported,<sup>9</sup> the signal to noise ratio of the spectra has been substantially improved in this experiment. The quantitative analysis of the emission spectra observed will be published elsewhere.

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## Photoaddition Reactions of Some Alkynes to Duroquinone and Photochemical Transformation of the Photoadducts

Sung Sik Kim\*, Ae Rhan Kim, Dong Jin Yoo†, and Sang Chul Shim†

*Department of Chemistry, Chonbuk National University, Chonju 560-756, Korea*

*†Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea*

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Quinones are an important class of compounds in organic synthesis, in industry, and in nature.<sup>1</sup> Due to their various spectroscopic properties and reactivities, the photochemistry of quinones has been a subject of interest in many areas.<sup>2-4</sup> Photoaddition of *p*-quinones to alkynes yields quinone methides, via an unstable intermediate spiro-oxetenes.<sup>5-6</sup> The *p*-quinones also add to a conjugated diyne such as 1,4-diphenylbutadiyne to give 1:1 adducts.<sup>7</sup>

In connection with our investigation of the scope of these reactions, we examined the photochemical reaction of duroquinone **1** having four electron-donating methyl groups with some alkynes, such as phenylacetylene **2**, diphenylacetylene **5**, 1,4-diphenylbutadiyne **9**, and 1,4-diethynylbenzene. It was observed that alkynes added to carbon-carbon double bond of duroquinone **1** to give [2+2] photocycloadducts, most of which are converted photochemically into their corresponding eight-membered compounds.

Preparative photochemical reactions were conducted in a photochemical reactor composed of a water-cooled system and a Pyrex (or a quartz) reaction vessel with 300 nm (or 254 nm) UV lamps (Rayonet Photochemical Reactor, Model RPR-208). Irradiation (300 nm) of duroquinone **1** (164 mg, 1.0 mmol) and excess of phenylacetylene **2** (2.0 mL) in dichloromethane (200 mL) for 25 h afforded the electrocyclic reaction product **4**<sup>8</sup> via [2+2]-photocycloadduct **3** which was not found in the photoreaction mixture using <sup>1</sup>H NMR spectroscopy. This reaction may reflect  $\pi, \pi^*$  activity in the excited duroquinone **1** having electron-donating methyl groups, the direction of addition being controlled by stabilization in the more stable 1,4-diradical intermediate. Flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (9:1, v/v) as the eluents gave the adduct **4** in 55% yield, in which ca. 30% of duroquinone **1** was recovered. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of 1:1 adduct **4** showed a vinyl proton in eight-membered ring at  $\delta$  7.57 ppm. The