

Substitution Effect on Electronic Transition of Bi-substituted Benzyl-type Radicals: Symmetric Substitution[†]

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Received June 18, 2007

A substitution effect on the electronic transition of bi-substituted benzyl-type radicals was discovered. The origin of the electronic $D_1 \rightarrow D_0$ transition of benzyl-type radicals was red-shifted upon substitution to the benzene ring. For symmetric bi-substituted benzyl-type radicals, it was found that the predicted shift obtained from mono-substituted benzyl-type radicals agreed well with the observation. The reason for this agreement is believed that the substituent contributes independently to the electronic energy. The substitution effect was applied to the symmetric bi-substituted difluoro-, dichloro- and dimethylbenzyl radicals.

Key Words : Spectroscopy, Benzyl-type radical, Substitution effect

Introduction

Accurate knowledge on electronic properties is of key importance in understanding the reactivity and structure of benzyl-type radicals, large conjugate organic radicals. The benzyl radical is a prototypical aromatic free radical¹ that has been believed to play an important role in aromatic chemical reaction as a reaction intermediate.

In benzyl-type radicals having substituents in the benzene ring, the electronic interaction between the substituents and the benzene ring should undoubtedly be of second order compared with that between the methylene group and the benzene ring, since such molecules have a planar structure,² with 7 delocalized π electrons, in which the CH_2 group contributes an electron.

The electronic structure of benzyl-type radicals should exhibit a close relationship to that of the benzyl radical, and one might be able to relate the two lowest-lying excited electronic states, $2^2\text{B}_2(\text{D}_2)$ and $1^2\text{A}_2(\text{D}_1)$ of benzyl-type radicals to those of the parental benzyl radicals.³ The weak visible emission from benzyl-type radicals is believed to arise from transitions to the 1^2B_2 ground electronic state from the close-lying 2^2B_2 and 1^2A_2 excited electronic states, whose energies are also affected differently by ring substitution.

In this work, we have discovered a substitution effect on the electronic transition of bi-substituted benzyl-type radicals. The origin of the electronic $D_1 \rightarrow D_0$ transition of benzyl-type radicals was red shifted upon substitution to the benzene ring, in which the size of the shift could be predicted from that of mono-substituted benzyl-type radicals.

Experimental

The benzyl-type radicals were formed and vibronically

excited in a corona excited supersonic expansion (CESE) from corresponding precursors seeded in a large amount of inert carrier gas. Although the mechanism for generation of benzyl-type radicals has not been exactly established, it is quite possible that the hot electrons formed in a corona discharge excite the most abundant species, that is, the carrier gas helium, and that the metastable helium atom in turn generates a vibronically excited benzyl-type radical in collision with the precursor, in which process the radicals are formed over a wide range of vibronic states. By contrast, inert carrier gas acts as an energy quencher during the free expansion process, producing electronically excited but rovibrationally cold species.⁴

Supersonic free jet expansion has been known as a powerful spectroscopic technique for the observation of molecular spectra in the gas phase.⁵ The spectral simplification and stabilization of transient species associated with the expansion of inert carrier gas cannot be obtained in any other way. The combination of the supersonic expansion technique with emission spectroscopy has had an enormous influence on the repertoire of spectroscopic studies of molecular species in the gas phase. Of the emission sources developed for these purposes, the prospective one providing enough continuous photon intensity for high resolution studies of weak transition is the pinhole-type glass nozzle,⁶ which has been employed for observation of the vibronic emission spectra of transient molecules.⁷ This nozzle has been applied to the vibronic emission spectra of many jet-cooled benzyl-type radicals in the gas phase.⁸⁻¹⁰

For many of the benzyl-type radicals, vibronic coupling between two close-lying D_1 and D_2 excited electronic states is so effective that observation of transitions originating from the D_2 excited electronic state cannot be obtained spectroscopically. Thus, the vibronic emission spectrum observed in the CESE scheme is similar to the single vibronic level dispersed fluorescence spectrum observed by pumping the origin band of the electronic transition.¹¹

[†]This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

Results and Discussion

The origin of the electronic $D_1 \rightarrow D_0$ transition of the benzyl radical has been determined by many spectroscopic techniques. Laser-induced fluorescence spectra¹² have identified the symmetry and position of the vibronic transition of the benzyl radical. The vibronic emission spectra¹³ show that the origin of the electronic $D_1 \rightarrow D_0$ transition is found at 22002 cm^{-1} . The same techniques have also been applied for observation of the vibronic spectra of mono-substituted methylbenzyl radicals, xylyl radicals. The origins of the *o*-, *m*-, and *p*-xylyl radicals were reported to be at 21345, 21485, and 21700 cm^{-1} , respectively, yielding a shift of 657, 517, and 302 cm^{-1} for each isomer.¹⁴

Although the origin of the $D_1 \rightarrow D_0$ transition of the 2,6-dimethylbenzyl radical, in the vibronic emission spectrum,¹⁵ has been reported to be located at $21,164 \text{ cm}^{-1}$, our revised analysis¹⁶ indicates that the bands at 20,616 and $21,164 \text{ cm}^{-1}$ should be the origin bands of the $D_1 \rightarrow D_0$ and the $D_2 \rightarrow D_0$ transitions, respectively, because the same vibrational structures in the ground state were identified. The observation of the transition, with appreciable intensity, from the D_2 state, suggests a weak vibronic coupling between the two excited electronic states. The substitution of two methyl groups at the *ortho*-position shifts the origin to the red region by 1386 cm^{-1} because the substituents shift the two electronic energies differently. Is there any way to predict the position of the origin of the electronic transition of bi-substituted benzyl-type radicals? We discovered that the shift obtained from the *o*-xylyl radical can be applied to the 2,6-dimethylbenzyl radical. Simply by subtracting the shift from the benzyl radical, we obtained the value of 20688 cm^{-1} , which agreed with the observation.

For application to another symmetric substitution, we have recently observed the vibronic emission spectrum of the jet-cooled fluorobenzyl radicals in CESE.¹⁷ Fluorobenzyl radicals are well known for their strong intensity of

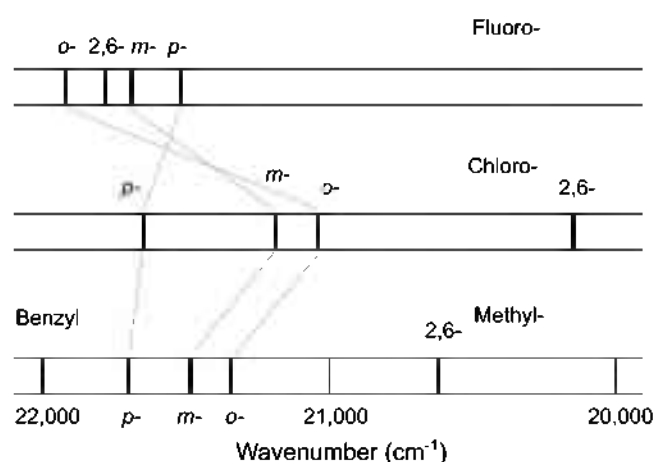


Figure 1. The tendency of the origin band of substituted benzyl radicals, fluorobenzyl, chlorobenzyl, and methylbenzyl radicals together with bi-substituted benzyl radical, 2,6-substituted benzyl radicals. The origin band of all benzyl-type radicals was shifted to red region upon substitution.

Table 1. List of the origin bands of the electronic $D_1 \rightarrow D_0$ transition of benzyl-type radicals with different substituents^a

Molecules	<i>o</i> -Isomer ^b	<i>m</i> -Isomer ^b	<i>p</i> -Isomer ^b	2,6-Substituted ^c
Fluorine	21924 (78)	21691 (311)	21527 (475)	21774 (21846)
Chlorine	21040 (962)	21194 (808)	21645 (357)	20153 (20078)
Methyl	21345 (657)	21485 (517)	21700 (302)	20616 (20688)

^aIn units of wavenumber (cm^{-1}). ^bThe numbers in parentheses indicate the shift from the benzyl radical upon substitution. ^cThe numbers in parentheses indicate the calculated values using the substitution effect.

fluorescence. All three isomers of the fluorobenzyl radicals have been observed, not only by laser techniques but also in CESE experiments. The *o*-, *m*-, and *p*-fluorobenzyl radicals^{11,18,19} show origin bands at 21924, 21691, and 21527 cm^{-1} , respectively, which corresponds to a shift from the benzyl radical of 78, 311, and 475 cm^{-1} for each isomer. The shift from the *o*- to *p*-isomers shows the reverse tendency from those of the chlorobenzyl and xylyl radicals as shown in Figure 1.

In this laboratory, we have observed, for the first time, the vibronic emission spectrum of the jet-cooled 2,6-difluorobenzyl radical.²⁰ The spectrum was analyzed according to the transition frequency and the bandshape, different bandshapes being obtained for different vibrational modes. The origin of the $D_1 \rightarrow D_0$ electronic transition was assigned to the most intensive band at 21774 cm^{-1} , showing the shift of 228 cm^{-1} from the benzyl radical. The shift was calculated to be only 156 cm^{-1} simply by adding two fluorine substitutions at the *ortho*-position. The agreement was also excellent for the symmetric difluorobenzyl radical.

Although the substitution of chlorine atoms significantly reduces the fluorescence intensity, we observed the vibronic emission spectra²¹⁻²³ of all three isomers of the chlorobenzyl radicals generated from corresponding chlorotoluenes in a CESE using a pinhole-type glass nozzle. The origins of the chlorobenzyl radicals were identified as the bands at 21040, 21194, and 21645 cm^{-1} , respectively, for the *o*-, *m*-, and *p*-isomers, representing shifts from the benzyl radicals of 962, 808, and 357 cm^{-1} respectively. Of the three isomers, the *o*-isomer showed the largest shift from the benzyl radical which result is different from that for fluorine-substituted benzyl radicals. We cannot exactly explain the physical reason for this different tendency, because all halogen atoms have an electronic withdrawing character.

The origin band of the 2,6-dichlorobenzyl radical²⁴ was observed to have the strongest intensity at 20153 cm^{-1} , red shifted by 1849 cm^{-1} from benzyl radical. The largest shift from chlorine substitution has been observed at the *ortho*-position. The shift, with the substitution effect, was calculated to be 1924 cm^{-1} , which was in excellent agreement with the observation. The comparisons between the observation and the calculation for the different bi-substituted benzyl radicals are listed in Table 1. Further application of the substitution effect is necessary for justification of the rule.

Conclusions

The shift of the origin band of benzyl-type radicals, in the electronic $D_1 \rightarrow D_0$ transition, was determined from vibronic emission spectra observed in a CESE. The shift of the origin of bi-substituted benzyl-type radicals from the benzyl radical was compared with the calculation derived from a combination of mono-substituted benzyl-type radicals. The calculation agrees well with the observation for symmetric multi-substituted benzyl-type radicals of methyl, fluorine, and chlorine. That agreement may be attributed to the independent contribution of each substituent to the electronic energy of the molecules.

Acknowledgment. This work was supported by Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2006-311-C00336 and R14-2003-033-01002-0). This paper is dedicated to Professor Sang Chul Shim on the occasion of his honorable retirement.

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