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Properties of Excited Ketyl Radicals of Benzophenone Analogues Affected by the Size and Electronic Character of the Aromatic Ring Systems

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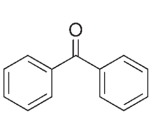
Abstract: The properties of benzophenone ketyl radical analogues with large aromatic ring systems, such as naphthylphenylketone (**2**), 4-benzoylbiphenyl (**3**), and bis(biphenyl-4-yl)methanone (**4**), were investigated in the excited state by using nanosecond–picosecond two-color two-laser flash photolysis. Fluorescence and transient absorption spectra of ketyl radicals of **2**–**4** in the excited state were observed for the first time. The fluorescence and properties of the excited ketyl radicals were significantly affected by the size and electronic properties of the aromatic ring systems. The reactivity of the ketyl radicals in the excited state with several quenchers was examined and they were found to show reactivity toward *N*,*N*-diethylaniline. In addition, for the benzophenone ketyl radical, a unique quenching process of the radical in the excited state by the ground-state parent molecule was found. The factors regulating the fluorescence lifetime of the ketyl radicals in the excited state are discussed quantitatively.

Keywords: benzophenone • flash photolysis • laser chemistry • photochemistry • radicals

Introduction

As free radials are one of the most important photochemical intermediates, radicals in the excited state are of interest in both photochemical and photophysical investigations.[1,2] The reactivity of the excited radical, which is different from that of the ground-state radical, and its emission are also attractive subjects.[3] The properties of the excited benzophenone (**1**) ketyl radical (**1H**$^\bullet$) and its related ketyl radicals have been extensively investigated.[3] In particular, a considerable number of studies of **1H**$^\bullet$ have been carried out by using absorption and emission spectroscopy to elucidate electronic structures and chemical properties in the condensed phase.

One of the attractive properties of **1H**$^\bullet$ is its highly emissive character. Fluorescence of other ketyl radicals as a result of the $D_1 \rightarrow D_0$ transition has also been detected in the condensed phase at room temperature. Establishing the factors that regulate the fluorescence lifetime of ketyl radicals is an interesting topic to investigate. It has been confirmed that the lifetime of derivatives of **1H**$^\bullet$ in the excited state increase with a decrease of the Stokes shift.[3h,s] Furthermore, it has been reported that anthrone and dibenzosuberone ketyl radicals in the excited state have long lifetimes owing to their structures, which prevent the conformational change between the D_0 and D_1 states.[3h,s] These experimental results indicate that the conformational change associated with the electronic transition between the D_1 and D_0 states plays an important role in the decay process. Based on these points, we decided to investigate the properties of ketyl radicals of benzophenone analogues with large aromatic ring systems, such as naphthylphenylketone (**2**), 4-benzoylbiphenyl (**3**), and bis(biphenyl-4-yl)methanone (**4**), in the excited state. Conformational change associated with the electronic transition between the D_1 and D_0 states should therefore be affected by the large aromatic ring systems of compounds **2**, **3**, and **4**.



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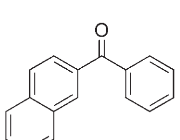

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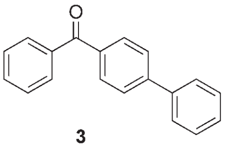

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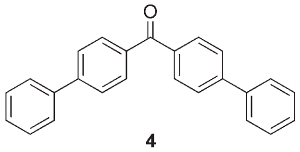

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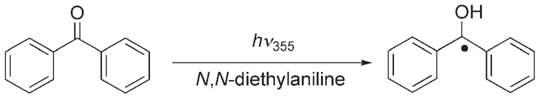
In the present work, the properties of the ketyl radicals of compounds **1**, **2**, **3**, and **4** (**1H**$^\bullet$, **2H**$^\bullet$, **3H**$^\bullet$, and **4H**$^\bullet$, respectively) have been investigated by using nanosecond–picosecond two-color two-laser flash photolysis. The fluorescence and transient absorption spectra of **2H**$^\bullet$(D_1), **3H**$^\bullet$(D_1), and **4H**$^\bullet$(D_1) have been observed for the first time. Factors that affect the lifetime of ketyl radicals in the excited state, such as uni- and bimolecular reactivities and conformational changes between the D_1 and D_0 states, are discussed quantitatively.

Results and Discussion

Generation of the ketyl radicals: **1H**$^\bullet$, **2H**$^\bullet$, **3H**$^\bullet$, and **4H**$^\bullet$ were generated by a bimolecular reaction with *N*,*N*-diethylaniline [Equation (1)].[4]



(1)

The spectra of the ketyl radicals are shown in Figure 1. The spectra of **1H**$^\bullet$, **3H**$^\bullet$, and **4H**$^\bullet$ are consistent with those reported in the literature.[3i,5] To the best of our knowledge, no report on the spectrum of **2H**$^\bullet$ exists. The absorption maxima (λ_a^{max}) of the ketyl radicals are summarized in Table 1.

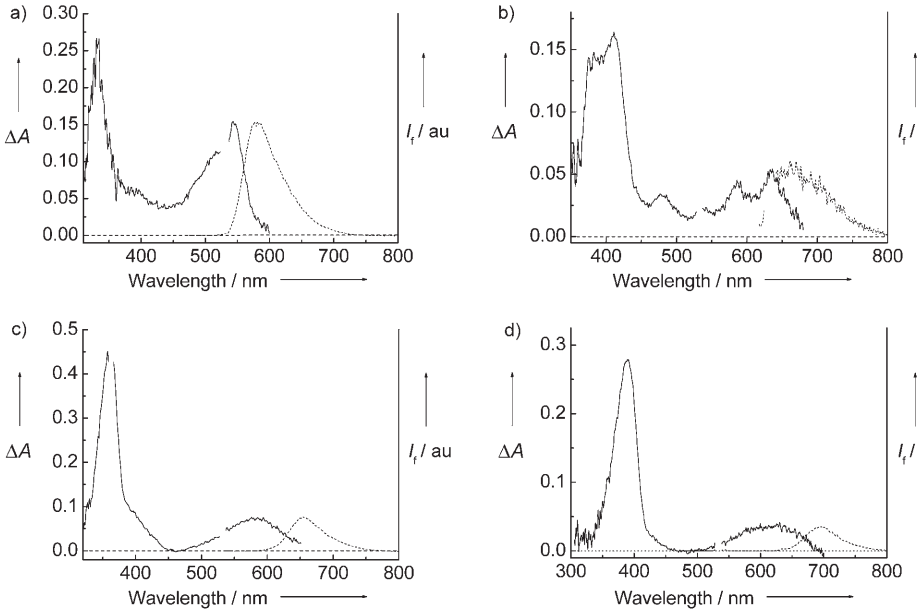


Figure 1. Absorption (——) and fluorescence (-----) spectra of a) **1H**$^\bullet$, b) **2H**$^\bullet$, c) **3H**$^\bullet$, and d) **4H**$^\bullet$ in argon-saturated acetonitrile at room temperature. The absorption spectra were obtained during the 355 nm one-laser flash photolysis of the corresponding parent molecules (1.0×10^{-4} M). The fluorescence spectra were obtained during the 355 and 532 nm two-color two-laser flash photolysis of the corresponding parent molecules (1.0×10^{-4} M). Both were carried out in the presence of *N*,*N*-diethylaniline (0.055 M). The blanks in the spectra around 355 and 532 nm are due to the residual second and third harmonic generation (SHG and THG) of the Nd^{3+}:YAG laser, respectively.

Table 1. Spectroscopic data for the ketyl radicals of compounds **1**–**4**.

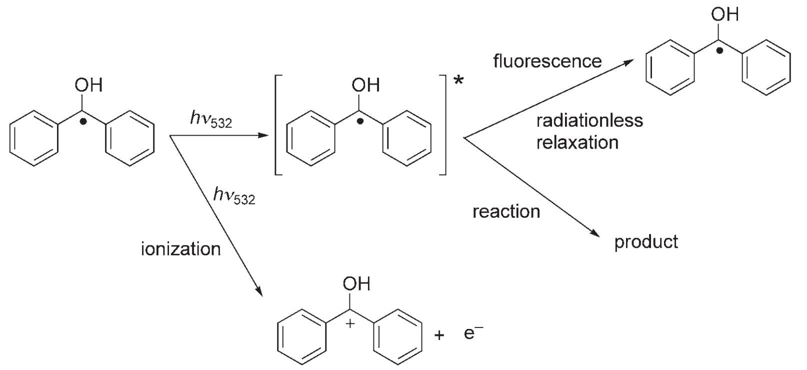
	λ_a^{max} [nm]	λ_f^{max} [nm]	λ_{D1}^{max} [nm]	$\nu_{ss}/10^3$ [cm^{-1}]	τ_{f0} [ns]	ΔE[a] [eV]
1	330, 545	582	345, 475	1.18	4.1 ± 0.2	2.1
2	411, 486, 541, 585, 636	661	≈450[b]	0.601	0.35	1.9
3	357, 585	656	389, 525	1.82	2.2	1.9
4	389, 630	696	462, 657	1.56	2.5	1.8

[a] The energy gap between the D_1 and D_0 states. [b] The peak was not clear due to the absorption overlap of **2H**$^\bullet$(D_1) and bleaching of **2H**$^\bullet$(D_0).

The absorption peaks of **1H**$^\bullet$ at $\lambda = 330$ and 545 nm were assigned to the $D_2 \leftarrow D_0$ and $D_1 \leftarrow D_0$ transitions, respectively.[3e,f] **3H**$^\bullet$ and **4H**$^\bullet$ showed analogous absorption spectra to **1H**$^\bullet$ (Figure 1).[5] The absorption peaks due to the $D_2 \leftarrow D_0$ and $D_1 \leftarrow D_0$ transitions of **3H**$^\bullet$ showed redshifts of 27 and 40 nm, respectively, relative to those of **1H**$^\bullet$, whereas the absorption peaks of **4H**$^\bullet$ showed an even greater redshift. It seems that phenyl substitution increases the redshift of the absorption peak of ketyl radicals. Compared with **1H**$^\bullet$, **3H**$^\bullet$, and **4H**$^\bullet$, **2H**$^\bullet$ shows five peaks in the spectral range (these bands have not been assigned), which indicate that a number of transitions participate in its absorption spectrum.

Fluorescence spectra and the lifetime of ketyl radicals: The generated ketyl radicals were excited at the visible absorption band by using a second laser (532 nm, 15 mJ pulse^{-1}, 30 ps fwhm) with a delay time of 1 μs after the first laser [Equation (2)].

Upon excitation, **1H**$^\bullet$ showed fluorescence. The fluorescence peak at $\lambda = 582$ nm (**1H**$^\bullet$(D_1)) in acetonitrile agreed well with that reported in the literature.[3i] The fluorescence spectrum of **1H**$^\bullet$(D_1) is almost a mirror image of the absorption spectrum (Figure 1). Although the same experiment was carried out in the presence of several concentrations of *N*,*N*-diethylaniline, the shape of the fluorescence spectrum did not change (Figure 2). Thus, it can be concluded that the interaction between **1H**$^\bullet$(D_1) and *N*,*N*-diethylaniline can be ignored under the present experimental conditions. Similar experimental results were described by Obi et al. who reported that **1H**$^\bullet$(D_0) forms a nonemissive complex with triethylamine due to hydrogen-bond formation, and that fluorescence is derived from free **1H**$^\bullet$.[6]



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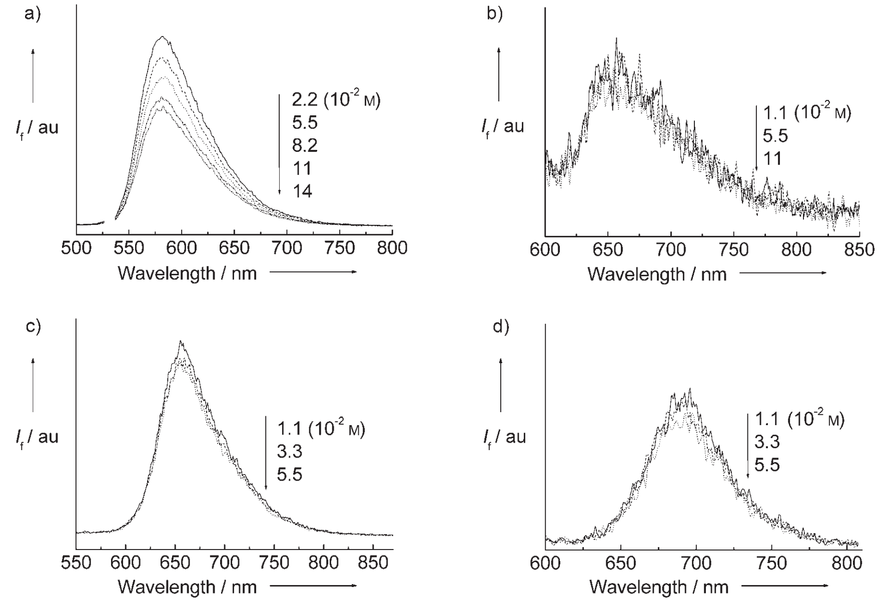


Figure 2. Fluorescence spectra of the ketyl radicals a) **1H**$^{\bullet}$, b) **2H**$^{\bullet}$, c) **3H**$^{\bullet}$, and d) **4H**$^{\bullet}$ during the 355 and 532 nm two-color two-laser flash photolysis of the corresponding parent molecules (1.0×10^{-4} M) in argon-saturated acetonitrile with different concentrations of *N*,*N*-diethylaniline.

The fluorescence peak of **1H**$^{\bullet}$(D$_1$) in cyclohexane at room temperature occurred at $\lambda = 565$ nm,[3s] which is blueshifted by 17 nm relative to that in acetonitrile. It seems that the properties of **1H**$^{\bullet}$(D$_1$) are significantly affected by the solvent polarity. Analogous fluorescence behavior was observed in the case of the other ketyl radicals. The fluorescence maxima (λ_f^{max}) and Stokes shift (ν_{ss}) values of the ketyl radicals are listed in Table 1. Among **1H**$^{\bullet}$, **3H**$^{\bullet}$, and **4H**$^{\bullet}$, the ν_{ss} value tends to be larger as the size of the phenyl ring system increases. It is therefore suggested that the large aromatic ring systems of **3H**$^{\bullet}$(D$_1$) and **4H**$^{\bullet}$(D$_1$) augment the difference between the conformations in the D$_0$ and D$_1$ states. This tendency seems to be limited to the ketyl radicals composed of phenyl and biphenyl groups. **2H**$^{\bullet}$ showed a smaller ν_{ss} value in spite of its aromatic ring. One of the possible reasons for this small conformational change is the delocalization of the spin density in the naphthalene ring. It has been reported that the spin density at the hydroxy-bearing carbon atom of **1H**$^{\bullet}$ is shifted substantially to a *para* position in the D$_1$ state.[3x] In the case of **2H**$^{\bullet}$(D$_1$), the shifted spin density would be delocalized in the naphthalene ring. As a result, the conformational change of **2H**$^{\bullet}$ between the D$_0$ and D$_1$ states would be smaller than those of **1H**$^{\bullet}$, **3H**$^{\bullet}$, and **4H**$^{\bullet}$.

The energy gap between the D$_1$ and D$_0$ states of **1H**$^{\bullet}$ (ΔE(D$_1$–D$_0$)) was determined from the fluorescence maxima (Table 1). The ΔE(D$_1$–D$_0$) values were found to decrease as follows: **1H**$^{\bullet}$ > **2H**$^{\bullet}$ = **3H**$^{\bullet}$ > **4H**$^{\bullet}$.

The fluorescence lifetimes (τ_f) of the ketyl radicals in the excited state were measured at the peak positions of the fluorescence spectra. All fluorescence decay curves fitted well with the single-exponential decay function (Figure 3). It has been reported that **1H**$^{\bullet}$(D$_1$) reacts with amine,[3g] and it was found that the τ_f values of **1H**$^{\bullet}$(D$_1$) decreased with an increase of the concentration of **1**(S$_0$). Thus, the intrinsic fluorescence lifetime (τ_{f0}) was estimated from the liner correlation between $1/\tau_f$ versus the concentration of *N*,*N*-diethylaniline ([*N*,*N*-diethylaniline]), and from $1/\tau_f$ versus the concentration of the parent molecules ([S$_0$]) according to Equation (3) (Figures 4 and 5):[1]

$$\frac{1}{\tau_f} = \frac{1}{\tau_{f0}} + k_{sq}[S_0] + k_q[N,N\text{-diethylaniline}] \tag{3}$$

in which k_q and k_{sq} denote the bimolecular reaction rate constants for the reaction with *N*,*N*-diethylaniline and the parent molecule, respectively. The τ_{f0} values of **1H**$^{\bullet}$(D$_1$), **2H**$^{\bullet}$(D$_1$), **3H**$^{\bullet}$(D$_1$), and **4H**$^{\bullet}$(D$_1$) are listed in Table 1.

The k_q value of **1H**$^{\bullet}$(D$_1$) was estimated to be 9.9×10^8 M^{-1}s^{-1} (Table 2). The k_q values of the other ketyl radicals in the excited state are summarized in Table 2. Radicals **2H**$^{\bullet}$(D$_1$), **3H**$^{\bullet}$(D$_1$), and **4H**$^{\bullet}$(D$_1$) have larger k_q values than that of **1H**$^{\bullet}$(D$_1$). The reaction distance between two molecules was expressed as the sum of the radius of each molecule. The Onsager radius of **2H**$^{\bullet}$, **3H**$^{\bullet}$, and **4H**$^{\bullet}$ is larger than that of **1H**$^{\bullet}$, and the reaction distance increases with increas-

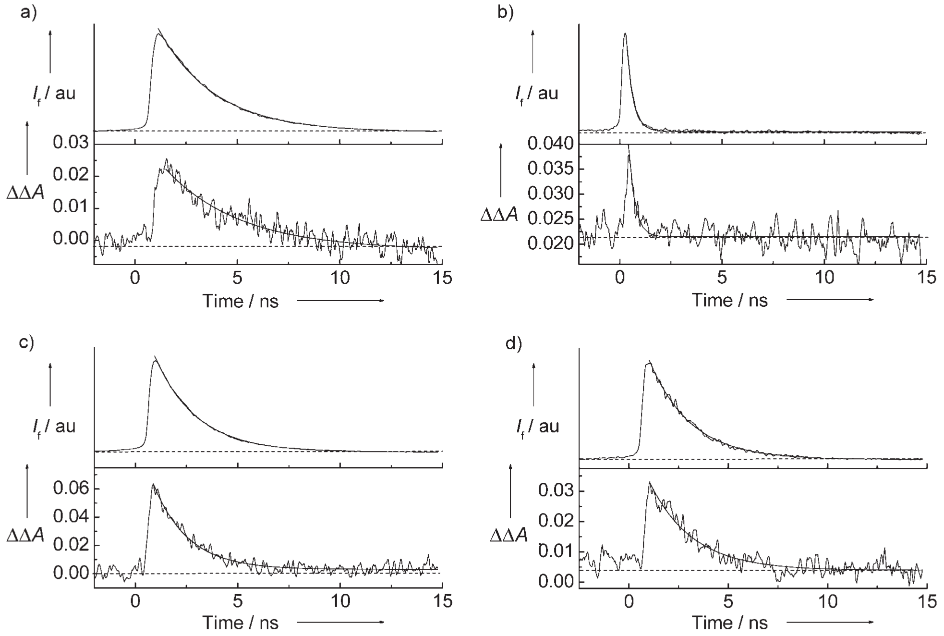


Figure 3. Kinetic traces for the fluorescence intensity and absorption of a) **1H$^\bullet$** ([*N*,*N*-diethylaniline] = 0.28 M), b) **2H$^\bullet$** ([*N*,*N*-diethylaniline] = 0.28 M), c) **3H$^\bullet$** ([*N*,*N*-diethylaniline] = 0.055 M), and d) **4H$^\bullet$** ([*N*,*N*-diethylaniline] = 0.055 M) at the peak position of fluorescence during the two-color two-laser photolysis of the corresponding parent molecules (1.0×10^{-4} M) in argon-saturated acetonitrile.

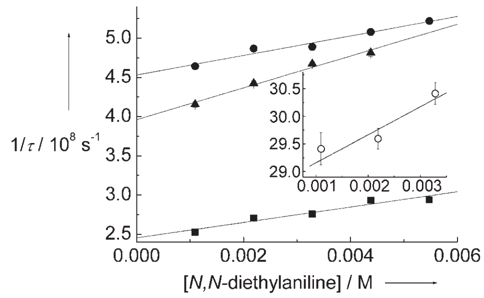


Figure 4. The plots of $1/\tau$ of **1H$^\bullet$** (■), **2H$^\bullet$** (○), **3H$^\bullet$** (▲), and **4H$^\bullet$** (●) versus [*N*,*N*-diethylaniline].

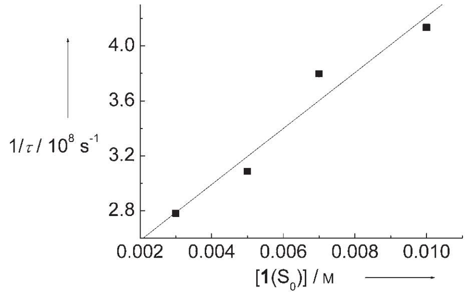


Figure 5. The plots of $1/\tau$ versus [$\mathbf{1}(S_0)$].

ing radius of the ketyl radical. Thus, it was suggested that an increase of the reaction distance between the ketyl radical and the *N*,*N*-diethylaniline molecules enhances the bimolecular reaction. The k_{sq} value was estimated to be $2.1\times10^{10}\,\mathrm{M^{-1}s^{-1}}$ for **1H$^\bullet$**(D_1), which is similar to the diffusion-controlled rate constant in acetonitrile. In our previous paper, electron transfer from the 4,4′-dimethoxybenzophenone ketyl radical in the D_1 state to the ground-state parent molecule was reported.[3w] As **1H$^\bullet$**(D_0) has quite a low oxidation potential ($E_{ox} = -0.25$ V versus SCE),[7] the electron transfer from **1H$^\bullet$**(D_1) to **1**(S_0) would occur (see below). For **2H$^\bullet$**(D_1), **3H$^\bullet$**(D_1), and **4H$^\bullet$**(D_1), no decrease of τ_f was observed with an increase of the ground-state parent molecule concentration. Because reduction potentials of **2**(S_0) ($E_{red} = -1.6$ V versus SCE)[8a] and **3**(S_0) ($E_{red} = -1.35$ V versus SCE)[8b] were more positive than that of **1**(S_0) ($E_{red} = -1.8$ V versus SCE), the inefficient electron transfer from **2H$^\bullet$**(D_1) and **3H$^\bullet$**(D_1) to the corresponding parent molecules indicates high oxidation potentials of **2H$^\bullet$**(D_0) and **3H$^\bullet$**(D_0). It should be noted that low solubility of **4H$^\bullet$** in acetonitrile ($<10^{-5}$ M) made the concentration-dependence experiment impossible. Even if **4H$^\bullet$**(D_1) reacts with **4**(S_0) at the diffusion-controlled rate constant, the difference of τ_f (<0.01 ns) is smaller than the experimental error.

Table 2. Rate constants of unimolecular and bimolecular chemical reactions (k_C), nonradiative (k_{nr}) and radiative (k_r) transition processes, and quenching by *N*,*N*-diethylaniline (k_q) and the ground-state parent molecule (k_{sq}).

	k_q [M^{-1}s^{-1}]	k_{sq} [M^{-1}s^{-1}]	k_r+k_{nr} [s^{-1}]	k_c [s^{-1}]
1	9.9×10^8	2.1×10^{10}	[b]	[b]
2	$(4.5\pm1.7)\times10^9$	[a]	[c]	[c]
3	1.2×10^9	[a]	2.9×10^8	1.4×10^8
4	2.1×10^9	[a]	3.6×10^8	5.3×10^6

[a] Quenching by the ground-state parent molecule was not observed under the present experimental conditions. [b] The recovery was not observed due to the absorption overlap of **1H$^\bullet$**(D_1). [c] The recovery was not observed under the present experimental conditions.

It is generally accepted that τ_{f0} of derivatives of **1H$^\bullet$**(D_1) becomes longer with a decrease of ν_{ss}.[3h,s] This tendency is also confirmed for **1H$^\bullet$**(D_1), **3H$^\bullet$**(D_1), and **4H$^\bullet$**(D_1). It is noteworthy that the τ_{f0} value of **2H$^\bullet$**(D_1), which showed the smallest ν_{ss}, was the shortest of the investigated ketyl radicals in the excited state.

Absorption spectra of the excited ketyl radicals: Immediately after the second laser irradiation of **1H$^\bullet$**(D_1), a sharp absorption band at $\lambda = 400$ nm and broad absorption bands at

$\lambda = 420$–520 and 600–800 nm appeared (Figure 6). As the lifetime of the band at 420–520 nm was essentially the same as the τ_f value, this can be attributed to $\mathbf{1H^{\bullet}}(D_1)$ (Figure 3). The transient absorption spectrum of $\mathbf{1H^{\bullet}}(D_1)$ in acetonitrile was similar to that in cyclohexane.[3s] The spectral shape of ketyl radicals in the excited state is shown in Figure 6. These transient absorption bands are attributed to the $D_n \leftarrow D_1$ transitions ($n > 1$) (Scheme 1). It is interesting to note that the absorption spectra were significantly affected by the aromatic rings. The peak of the transient absorption spectrum in the visible region (λ_{D1}^{max}) was redshifted in the order of $\mathbf{4H^{\bullet}}(D_1) > \mathbf{3H^{\bullet}}(D_1) > \mathbf{1H^{\bullet}}(D_1)$. For $\mathbf{2H^{\bullet}}(D_1)$, only a weak, broad absorption band was observed around 450 nm.

The lifetimes of the bands at 400 and 600–800 nm of $\mathbf{1H^{\bullet}}(D_1)$ were longer than τ_f. These peaks were proposed to be those of the benzophenone radical anion ($\mathbf{1^{\bullet -}}$). It is sug-

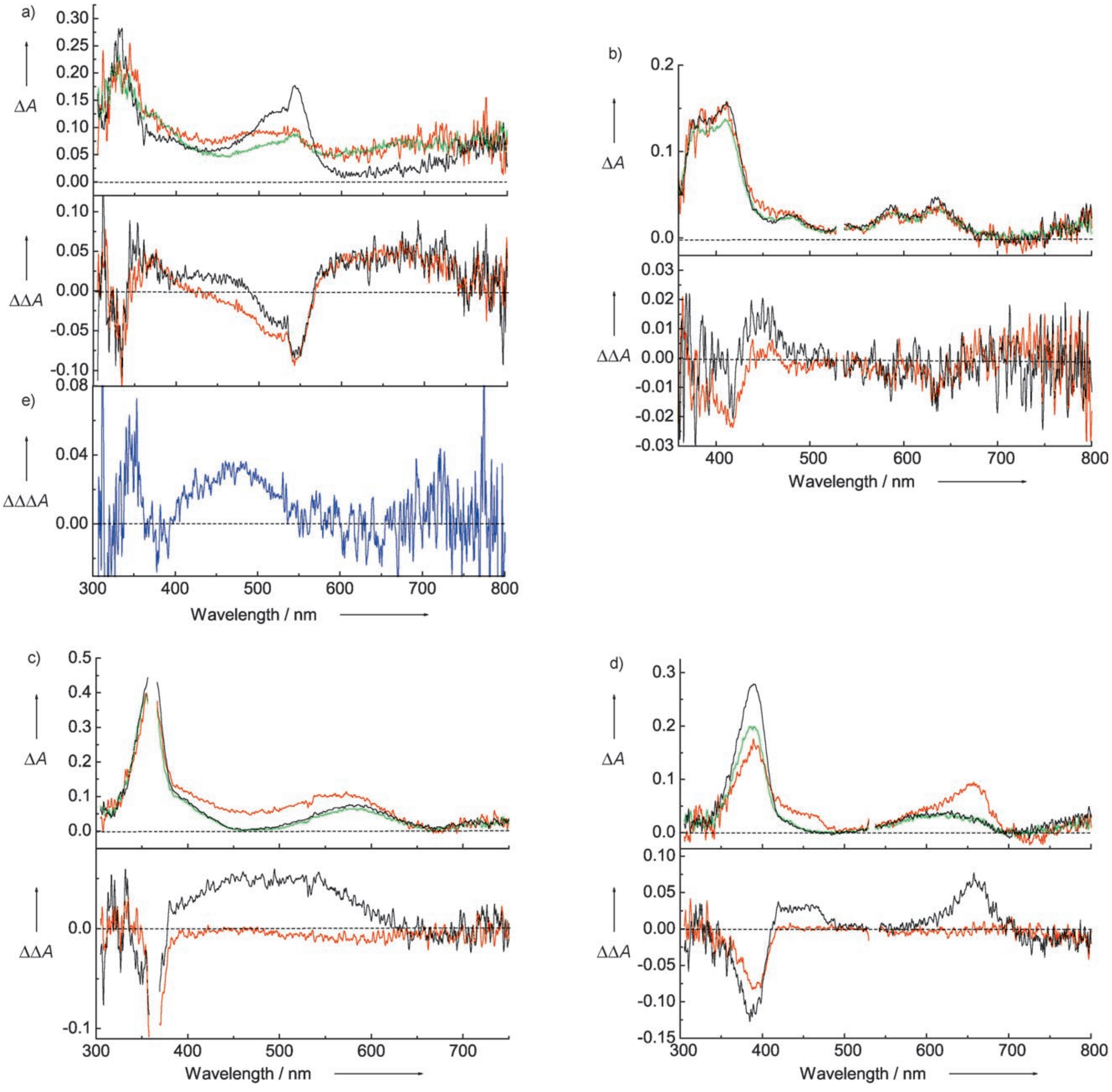
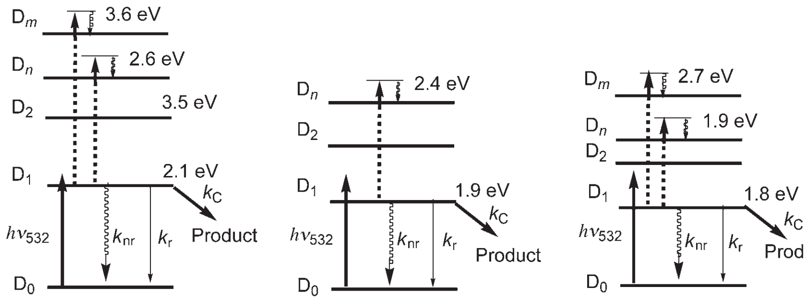


Figure 6. Transient absorption spectra (upper spectra) observed at 0.5 (red line) and 20 ns (green line) after the second laser irradiation during the two-color two-laser photolysis (266 or 355 and 532 nm), and the spectrum during one-laser photolysis (266 or 355 nm, black line) of a) **1** (1.0×10^{-4} M; [*N*,*N*-diethylaniline] = 0.28 M), b) **2** (1.0×10^{-4} M; [*N*,*N*-diethylaniline] = 0.28 M), c) **3** (1.0×10^{-4} M; [*N*,*N*-diethylaniline] = 0.055 M), and d) **4** (1.0×10^{-4} M; [*N*,*N*-diethylaniline] = 0.055 M) in argon-saturated acetonitrile. The second laser irradiated 1 µs after the first laser pulse. The transient absorption spectra of ketyl radicals in the D_1 state (lower spectrum, black line) were given by subtracting one spectrum (upper spectrum, black line) from the other (upper spectrum, red line). Changes in the transient absorption spectra of ketyl radicals in the D_0 state (lower spectrum, red line) at 20 ns after the second laser irradiation were given by subtracting one spectrum (upper spectrum, black line) from the other (upper spectrum, green line). In the case of $\mathbf{1H^{\bullet}}$, the transient absorption spectra of $\mathbf{1H^{\bullet}}(D_1)$ (e) was given by subtracting one spectrum (middle spectrum, red line) from the other (middle spectrum, black line). The blanks in the spectra around 355 and 532 nm were due to the residual SHG and THG of the Nd^{3+}:YAG laser, respectively.



Scheme 1. Energy-level diagrams of $\mathbf{1H^{\bullet}}$ (left), $\mathbf{3H^{\bullet}}$ (middle), and $\mathbf{4H^{\bullet}}$ (right) in the ground and excited states and the transient processes.

gested that both ionization and electron-transfer processes giving $\mathbf{1}^{\bullet-}$ occurred upon the second laser excitation. The former process generates $\mathbf{1}^{\bullet-}$ by a two-step mechanism: $\mathbf{1H^{\bullet}}$ is ionized by the irradiation of the second laser causing the ejection of an electron into the solvent. The solvated electron (e^-_{solv}) generated in acetonitrile is then trapped by $\mathbf{1}(S_0)$ to produce $\mathbf{1}^{\bullet-}$.[3e] The latter process is the above-mentioned electron transfer from $\mathbf{1H^{\bullet}}(D_1)$ to $\mathbf{1}(S_0)$.

For other ketyl radicals, no formation of radical anions was observed. Because e^-_{solv} has quite "high reducing power", the e^-_{solv} generated by the ionization of ketyl radicals should reduce the parent molecules in the ground state. Thus, it is suggested that the ionization process also did not occur in the cases of $\mathbf{2H^{\bullet}}$, $\mathbf{3H^{\bullet}}$, and $\mathbf{4H^{\bullet}}$, probably because their ionization potentials are higher than that of $\mathbf{1H^{\bullet}}$.

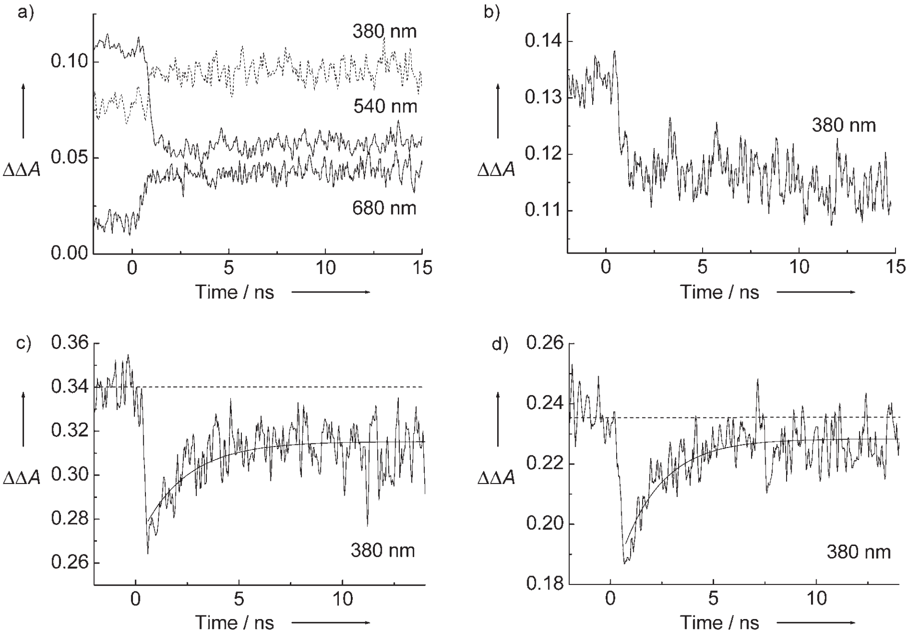


Figure 7. Recovery of absorption of a) $\mathbf{1H^{\bullet}}$ ([N,N-diethylaniline] = 0.28 M), b) $\mathbf{2H^{\bullet}}$ ([N,N-diethylaniline] = 0.28 M), c) $\mathbf{3H^{\bullet}}$ ([N,N-diethylaniline] = 0.055 M), and d) $\mathbf{4H^{\bullet}}$ ([N,N-diethylaniline] = 0.055 M) during the two-color two-laser photolysis of the corresponding parent molecules (1.0×10^{-4} M) in argon-saturated acetonitrile.

Upon excitation with the second laser, the bleaching and recovery of $\mathbf{3H^{\bullet}}(D_0)$ and $\mathbf{4H^{\bullet}}(D_0)$ were observed (Figure 7). In the cases of $\mathbf{1H^{\bullet}}$ and $\mathbf{2H^{\bullet}}$, only bleaching of the D_0 state was observed. The deactivation of the excited ketyl radical can also be attributed to the combination of a unimolecular chemical reaction (k_C), a self-quenching type of reaction with the ground-state parent molecules (k_{sq}), a reaction with N,N-diethylaniline (k_q), and nonradiative (k_{nr}) and radiative (k_r) transition processes (Scheme 1). The observed lifetime (τ) can be expressed as shown in Equation (4):

$$\tau = \frac{1}{k_r + k_{nr} + k_C + k_q[N,N\text{-diethylaniline}] + k_{sq}[S_0]} \tag{4}$$

Because the chemical reactions do not regenerate the D_0 state, the sum of k_r and k_{nr} is given by Equation (5):

$$1 - \frac{\Delta\Delta A(t=\infty)}{\Delta\Delta A} = (k_r + k_{nr})\tau \tag{5}$$

in which $\Delta\Delta A$ and $\Delta\Delta A(t=\infty)$ refer to the absorption immediately and a sufficiently long time after the second laser irradiation, respectively, as estimated from the curve fitting. The recovery rates of $\mathbf{3H^{\bullet}}(D_0)$ and $\mathbf{4H^{\bullet}}(D_0)$ after the bleaching upon the second laser irradiation were identical to the corresponding fluorescence lifetimes. These results strongly indicate that none of the products absorb photons at the examined wavelength. k_C can be estimated from Equation (6):

$$\frac{\Delta\Delta A(t=\infty)}{\Delta\Delta A} = (k_c + k_q[N,N\text{-diethylaniline}] + k_{sq}[S_0])\tau \tag{6}$$

The k_c and (k_r+k_{nr}) values for the ketyl radicals were estimated as summarized in Table 2. It is noteworthy that $\mathbf{2H^{\bullet}}$ had a much larger k_c value than the other compounds. In the case of $\mathbf{1H^{\bullet}}$, it has been reported that 20% of the chemical reaction process is photoionization and 80% is O–H bond cleavage to generate $\mathbf{1}(S_0)$.[3i] The chemical reaction is possible for $\mathbf{2H^{\bullet}}(D_1)$, $\mathbf{3H^{\bullet}}(D_1)$, and $\mathbf{4H^{\bullet}}(D_1)$. However, as the ionization of **2H**$^{\bullet}$(D$_1$), **3H**$^{\bullet}$(D$_1$), and **4H**$^{\bullet}$(D$_1$) was not observed under the present experimental conditions, it is suggested that the main chemical reaction process was the O–H bond cleavage. The optimized geometry of **2H**$^{\bullet}$(D$_1$) calculated at the HF/6-31G** level[9] is shown in Figure 8. The phenyl ring of **2H**$^{\bullet}$ is twisted and the hydrogen atom of the hydroxyl group is close to the phenyl ring in the excited state. The distance between these two parts was calculated to be 3.1 Å, which is suitable for OH–π hydrogen-bond formation between benzene and the alcohol.[10] It is suggested that the OH–π interaction promotes the O–H bond-cleavage process from **2H**$^{\bullet}$(D$_1$).

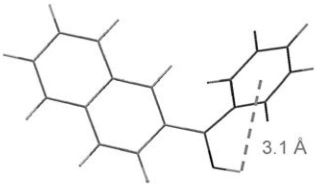


Figure 8. Optimized geometry of **2H**$^{\bullet}$(D$_1$).

The k_C value of **4H**$^{\bullet}$(D$_1$) is smaller than that of **3H**$^{\bullet}$(D$_1$). The O–H bond-cleavage process from **4H**$^{\bullet}$(D$_1$) is inefficient owing to the small conformational change between the D$_0$ and D$_1$ states. Because **4H**$^{\bullet}$(D$_1$) had a larger (k_r+k_{nr}) value than that of **3H**$^{\bullet}$(D$_1$), according to the energy-gap law we suggest that this difference reflects the difference of ΔE(D$_1$–D$_0$).[1]

Conclusion

In the present work, the properties of **1H**$^{\bullet}$(D$_1$), **2H**$^{\bullet}$(D$_1$), **3H**$^{\bullet}$(D$_1$), and **4H**$^{\bullet}$(D$_1$) were investigated by using nanosecond–picosecond two-color two-laser flash photolysis. The properties of these ketyl radicals in the excited state were significantly affected by the size and electronic properties of the aromatic ring systems. For **1H**$^{\bullet}$(D$_1$), **3H**$^{\bullet}$(D$_1$), and **4H**$^{\bullet}$(D$_1$), τ_{f0} becomes longer with a decrease of the ν_{ss} value. Although **2H**$^{\bullet}$ had a smaller ν_{ss} value than that of **1H**$^{\bullet}$, its τ_f value was shorter. It is suggested that the OH–π interaction in the excited state promotes the O–H bond-cleavage process of **2H**$^{\bullet}$(D$_1$). Bimolecular reactions between ketyl radicals in the excited state and several quenchers were observed. Ketyl radicals in the excited state showed reactivity with *N,N*-diethylaniline. It was found that **1H**$^{\bullet}$(D$_1$) was efficiently quenched by the ground-state parent molecule.

Experimental Section

The two-color two-laser flash photolysis experiments were carried out by using the third (355 nm) harmonic oscillation of a nanosecond Nd^{3+}:YAG laser (Quantel, Brilliant; 5 ns fwhm) as the first laser and the second harmonic oscillation (532 nm) of a picosecond Nd^{3+}:YAG laser (Continuum, RGA69-10; 30 ps fwhm, 10 Hz) as the second laser. A delay time of two laser flashes was adjusted to 1 μs by using a four channel digital delay/pulse generator (Stanford Research Systems, DG 535). The breakdown of Xe gas generated by the fundamental pulse of the second laser was used as a probe light. Transient absorption spectra and kinetic traces were measured by using a streak camera (Hamamatsu Photonics, C7700) equipped with a CCD camera (Hamamatsu Photonics, C4742-98) and were stored by using a personal computer. To avoid stray light and pyrolysis of the sample by the probe light, suitable filters were employed. Each sample was poured into a transparent rectangular quartz cell (1.0 × 0.5 × 2.0 cm) at room temperature.

Compounds **1**, **2**, **3**, and **4** were purchased from Kanto Chemical, Tokyo Kasei, Aldrich, and Lancaster, respectively. **1** was recrystallized from ethanol before use. The other compounds were used as received. Sample solutions were deoxygenated before irradiation by bubbling with argon gas for 30 min.

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[1] a) N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Melco Park, CA, **1978**; b) P. Suppan, *Chemistry and Light*, The Royal Society of Chemistry, Cambridge, **1994**.

[2] a) V. Ramamurthy, K. S. Schanze, *Molecular and Supramolecular Photochemistry Vol. 2*, Marcel Dekker, New York, **1994**; b) J. C. Scaiano, L. J. Johnston, W. G. McGimpsey, D. Weir, *Acc. Chem. Res.* **1988**, *21*, 22; c) M. Y. Melnikov, V. A. Smirnov, *Handbook of Photochemistry of Organic Radicals*, Begell House, New York, **1996**.

[3] a) B. W. Hodgson, J. P. Keene, E. J. Land, A. J. Swallow, *J. Chem. Phys.* **1975**, *63*, 3671; b) K. Razi Naqvi, U. P. Wild, *Chem. Phys. Lett.* **1976**, *41*, 570; c) K. Obi, H. Yamaguchi, *Chem. Phys. Lett.* **1978**, *54*, 448; d) H. Baumann, K. P. Schumacher, H. J. Timpe, V. Řehák, *Chem. Phys. Lett.* **1982**, *89*, 315; e) M. C. Thurnauer, D. Meisel, *Chem. Phys. Lett.* **1982**, *92*, 343; f) V. Nagarajan, R. W. Fessenden, *Chem. Phys. Lett.* **1984**, *112*, 207; g) H. Baumann, C. Merckel, H. J. Timpe, A. Graness, J. Kleinschmidt, I. R. Gould, N. J. Turro, *Chem. Phys. Lett.* **1984**, *103*, 497; h) H. Hiratsuka, T. Yamazaki, Y. Maekawa, T. Hikida, Y. Mori, *J. Phys. Chem.* **1986**, *90*, 774; i) L. J. Johnston, D. J. Lougnot, V. Wintgens, J. C. Scaiano, *J. Am. Chem. Soc.* **1988**, *110*, 518; j) R. W. Redmond, J. C. Scaiano, L. J. Johnston, *J. Am. Chem. Soc.* **1992**, *114*, 9768; k) M. R. Topp, *Chem. Phys. Lett.* **1976**, *39*, 423; l) J. C. Scaiano, M. Tanner, D. Weir, *J. Am. Chem. Soc.* **1985**, *107*, 4396; m) A. Bromberg, K. H. Schmidt, D. Meisel, *J. Am. Chem. Soc.* **1985**, *107*, 83; n) L. J. Johnston, J. C. Scaiano, *J. Am. Chem. Soc.* **1985**, *107*, 6368; o) S. Wada, Y. Matsushita, K. Obi, *J. Phys. Chem. A* **1997**, *101*, 2423; p) S. Hamatani, K. Tsuji, A. Kawai, K. Shibuya, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1370; q) E. F. Hilinski, D. Huppert, D. F. Kelley, S. V. Milton, P. M. Rentzepis, *J. Am. Chem. Soc.* **1984**, *106*, 1951; r) K. Tokumura, N. Mizukami, M. Udagawa, M. Itoh, *J. Phys. Chem.* **1986**, *90*, 3873; s) M. Sakamoto, X. Cai, M. Hara, S. Tojo, M. Fujitsuka, T. Majima, *J. Phys. Chem. A* **2004**, *108*, 8147; t) M. Sakamoto, X. Cai, M. Hara, S. Tojo, M. Fujitsuka, T. Majima, *J. Phys. Chem. A* **2005**, *109*, 2452; u) J. C. Netto-Ferreira, W. F. Murthy, R. W. Redmond, J. C. Scaiano, *J. Am. Chem. Soc.* **1990**, *112*, 4472; v) M. Sakamoto, X. Cai, M. Hara, S. Tojo, M. Fujitsuka, T. Majima, *J. Am. Chem. Soc.* **2005**, *127*, 3702; w) M. Sakamoto, X. Cai, M. Fujitsuka, T. Majima, *J. Phys. Chem. A* **2005**, *109*, 6830; x) W. Adam, F. Kita, R. S. Oestrich, *J. Photochem. Photobiol. A* **1994**, *80*, 187.

[4] a) Y. Matsushita, Y. Kajii, K. Obi, *J. Phys. Chem.* **1992**, *96*, 4455; b) S. Arimitsu, H. Masuhara, N. Mataga, H. Tsubomura, *J. Phys.*

Chem. **1975**, *79*, 1255; c) J. D. Simon, K. S. Peters, *J. Am. Chem. Soc.* **1983**, *105*, 4875; d) H. Miyasaka, K. Morita, K. Kamada, N. Mataga, *Chem. Phys. Lett.* **1991**, *178*, 504; e) H. Miyasaka, K. Morita, K. Kamada, T. Nagata, M. Kiri, N. Mataga, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3229; f) K. S. Peters, G. Kim, *J. Phys. Chem. A* **2004**, *108*, 2598.

[5] a) A. Kawai, T. Yamamoto, T. Okutsu, K. Obi, *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2625; b) J. D. Simon, K. S. Peters, *J. Phys. Chem.* **1983**, *87*, 4855.

[6] a) A. Kawai, M. Hirakawa, T. Abe, K. Obi, K. Shibuya, *J. Phys. Chem. A* **2001**, *105*, 9628; b) T. Abe, A. Kawai, Y. Kajii, K. Shibuya, K. Obi, *J. Phys. Chem. A* **1999**, *103*, 1457; c) A. Kawai, A. Aoki, Y. Kobori, K. Obi, *J. Phys. Chem.* **1996**, *100*, 10021; d) Y. Kajii, H. Itabashi, K. Shibuya, K. Obi, *J. Phys. Chem.* **1992**, *96*, 7244.

[7] T. Lund, D. D. M. Wayner, M. Jonsson, A. G. Larsen, K. Daasbjerg, *J. Am. Chem. Soc.* **2001**, *123*, 12590.

[8] a) T. Sato, M. Kubo, K. Nishigaki, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 815; b) R. O. Loutfy, R. W. Yip, S. K. Dogra, *Tetrahedron Lett.* **1977**, *33*, 2843.

[9] Calculations were performed by using Spartan02, Wavefunction, Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA92612.

[10] a) A. Fujii, T. Ebata, N. Mikami, *J. Phys. Chem. A* **2002**, *106*, 8554; b) S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami, K. Tanabe, *J. Am. Chem. Soc.* **2000**, *122*, 11450.

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