

## Fluorescence Properties of the Ketyl Radical from 10,10-Dimethylantrone: An Unusually Long Lived Excited Ketyl Radical†

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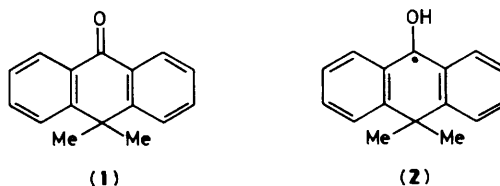
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The excited state of the ketyl radical from 10,10-dimethylantrone fluoresces with  $\lambda_{\text{max}} = 560$  nm and decays with a lifetime of 33 ns in toluene at room temperature.

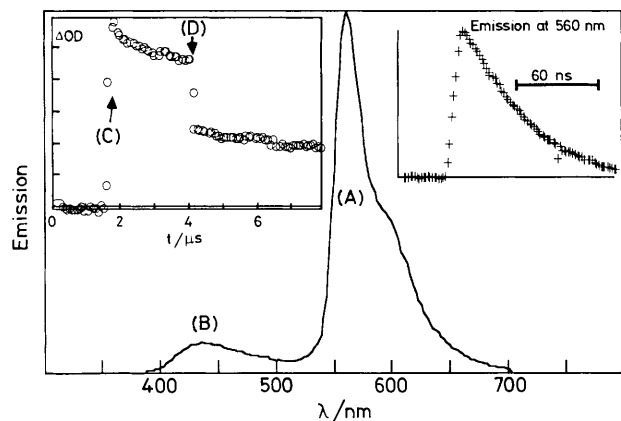
The photophysics and photochemistry of reaction intermediates are subjects of current interest. In the case of ketyl radicals several reports have been concerned with the fluorescence and lifetime from excited diarylketyl radicals. For the parent  $\text{Ph}_2\dot{\text{C}}\text{OH}$  radical typical fluorescence lifetimes are *ca.* 4 ns in solution at room temperature.<sup>1-10</sup> This short lifetime has been a limiting factor in time resolved studies of the chemical reactivity of excited free radicals of this type. We now report that by restricting the conformational flexibility of the ring system in the radical it is possible to extend dramatically the lifetime of the fluorescent state.

The solution photochemistry of 10,10-dimethylantrone (1) in the presence of hydrogen donors leads to the corresponding

ketyl radical (2). For example, the rate constant for triplet reaction with cyclohexane is  $7.6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>11</sup> The spectroscopic properties of the triplet state and of the ketyl radical are rather similar to those for the intermediates derived from other aromatic ketones such as benzophenone. *E.g.* (2) shows an absorption maximum at 535 nm, compared with 545 nm for  $\text{Ph}_2\dot{\text{C}}\text{OH}$ .<sup>9</sup>



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**Figure 1.** Doublet-douplet fluorescence (A) from (2) and phosphorescence (B) from (1) [monitored at point (D), see left insert] obtained by 308 + 337 nm excitation of 0.3 mM (1) in toluene. *Inserts:* (left) Transient absorption trace induced by 308 (C) + 337 nm (D) excitation for the same sample monitored at 360 nm and (right) decay of the fluorescence from (2) in  $[^2\text{H}_8]$ toluene, monitored at 560 nm.

Radical (2) was generated by laser irradiation (308 nm) of (1) in toluene.‡ Excitation of (2), with either a nitrogen (337 nm) or a dye (480 nm) laser, led to extensive bleaching of the radical absorption (see insert in Figure 1), similar to that observed previously with  $\text{Ph}_2\dot{\text{C}}\text{OH}$ .<sup>6,9</sup> Figure 1 shows the fluorescence spectrum of (2) ( $\lambda_{\text{max}} = 560$  nm) recorded in toluene at room temperature employing 337 nm excitation; the weak emission in the 400–500 nm region is due to phosphorescence from (1) induced by the nitrogen laser; these results are in line with those obtained for related radicals.<sup>8,9</sup> The lifetime of excited (2) at room temperature was 33 ns, *i.e.* much longer than those for typical ketyl radicals. Deuteriation at the hydroxylic position leads to a lifetime of 44 ns for (2)-OD in  $[^2\text{H}_8]$ toluene (see insert in Figure 1), suggesting that the O–H bond is directly involved in the decay process; the isotope effect is considerably smaller than that reported for diphenylketyl radicals.<sup>9,10</sup>

Excited (2) can be readily quenched by electron rich and electron deficient substrates. Table 1 shows the rate constants obtained in toluene; these are based on the shortening of the

‡ The details of the laser photolysis system and modifications for two-laser experiments have been reported elsewhere.<sup>12</sup>

**Table 1.** Quenching of excited (2) by various substrates in toluene at room temperature.

Quencher	$k_q$ ( $\text{M}^{-1}\text{s}^{-1}$ ) <sup>a</sup>
Triethylamine	$1.4 \times 10^9$
Propan-2-ol	$9.3 \times 10^8$
Methyl methacrylate	$3.9 \times 10^8$
1,4-Cyclohexadiene	$\leq 10^6$

<sup>a</sup> Typical error  $\pm 20\%$ .

fluorescence lifetimes by the substrates. 1,4-Cyclohexadiene, an excellent hydrogen donor, is a very poor quencher. This suggests that excited (2) is a very poor hydrogen abstractor in spite of the favourable enthalpic change that would be involved in hydrogen abstraction by the excited radical. The data for methyl methacrylate suggests that the electron donor ability of excited (2) is intermediate between those of excited  $\text{Ph}_2\dot{\text{C}}\text{H}$  ( $k = 4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ )<sup>12a</sup> and  $\text{Ph}_2\dot{\text{C}}\text{OH}$  ( $2.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>7</sup>

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