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# Picosecond Spectroscopic Characterization of the 9-Fluorenyl Cation in Solution

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In recent time-resolved spectroscopic studies of the twisted excited singlet state ($^1p^*$) of tetraphenylethylene,[1] the absorption spectrum of $^1p^*$ was considered in terms of diphenylmethyl cation and anion chromophores. For our studies of 9,9′-bifluorenylidene,[1b] a comparison of the time-dependent spectra could be made with spectra of the 9-fluorenyl (**1**) anion[2] and $\mathbf{1}^\bullet$.[3] The assignment[4a] of the absorption spectrum of $\mathbf{1}^+$ is less well-established, and reasons for cautions consideration of the assignment have been provided.[4b] On the basis of the recent work of Wan and co-workers,[5] the reports of spectroscopic observations of arylmethyl cations from photodissociations of carbon–halogen bonds,[6] and the results described herein, we have demonstrated that 9-fluorenol (**1**-OH), 9-chlorofluorene (**1**-Cl), and 9-methyl-9-fluorenol (**2**-OH) are photochemically converted, under suitable conditions, to carbocations which can be characterized via picosecond absorption spectroscopy.[7]

When **1**-OH is excited in a 9:1 (v:v) mixture of $H_2O/CH_3OH$, an absorption band at 515 nm and a weaker, broad band near 610 nm (Figure 1a) appear promptly, i.e., within the time duration of the 30-ps, 266-nm excitation pulse, and decay with time constants ($\tau_d$) of < 20 ps, the shortest time constant that can be resolved in these experiments. For a 1:1 $H_2O/CH_3OH$ solvent mixture, the two bands, now of almost equal intensity (Figure 1b), appear promptly and decay with $\tau_d < 20$ ps. With methanol as solvent, absorption throughout the 400–760-nm region of interrogation appears promptly and exhibits a 620-nm maximum which is more intense than a 460-nm maximum (Figure 1c). The 620-nm band decays to ~10% of its maximum intensity within 1.0 ns after excitation, and a pair of weak, sharp bands at 470 and 500 nm, which are assigned to $\mathbf{1}^\bullet$,[3] appear. These absorption bands of $\mathbf{1}^\bullet$ can be discerned as early as 75 ps postexcitation and persist for times as long as 20 ns, the maximum time after excitation probed in these experiments. Similar time-dependent spectral behavior (Figure 1d) is observed for **1**-OH in $CH_3CN$ except that the promptly appearing absorption maxima occur near 450 and 625 nm and, in addition to the presence of the 470- and 500-nm bands at 20 ns after excitation, an absorption which extends from <400 nm is observed. When **1**-Cl is excited at 266 nm in 3:2 $H_2O/CH_3OH$, a stronger band at 515 nm and a weaker band near 615 nm (Figure 1e) appear promptly and decay ($\tau_d < 20$ ps).

Deno et al.[4a] reported absorption maxima at 655 and 484 nm with $\epsilon_{655}/\epsilon_{484} = 1.51$ for $\mathbf{1}^+$ generated from **1**-OH in sulfuric acid. More recently, Olah et al.[4b] reported inconclusive results for the generation of $\mathbf{1}^+$ under the conditions of Deno et al.[4a] and were unable to generate $\mathbf{1}^+$ from several possible precursors in superacidic media. Our transient spectra recorded after excitation of **1**-OH in $H_2O/CH_3OH$ mixtures reveal the presence of two absorption bands whose relative intensities depend on solvent polarity. The spectrum illustrated in Figure 1b can be considered to be a weighted average of the spectra illustrated in Figure 1 (parts a and c). It was under conditions in which water was added to methanol that Wan and co-workers observed the greatest efficiency for photomethanolysis of **1**-OH.[5,16] When **1**-Cl is excited in 3:2 $H_2O/CH_3OH$, the promptly appearing 515-nm absorption band is the same as that resulting from excitation of **1**-OH in 9:1 or 1:1 $H_2O/CH_3OH$. Our picosecond absorption data indicate that the previous assignment[4a] of the two absorption bands to $\mathbf{1}^+$ is incorrect and lead us to assign the 515-nm band *alone* to $\mathbf{1}^+$ and the absorption with a maximum near 615 nm and a weaker one near 450 nm to transitions originating from $S_1$ of **1**-OH.[8]

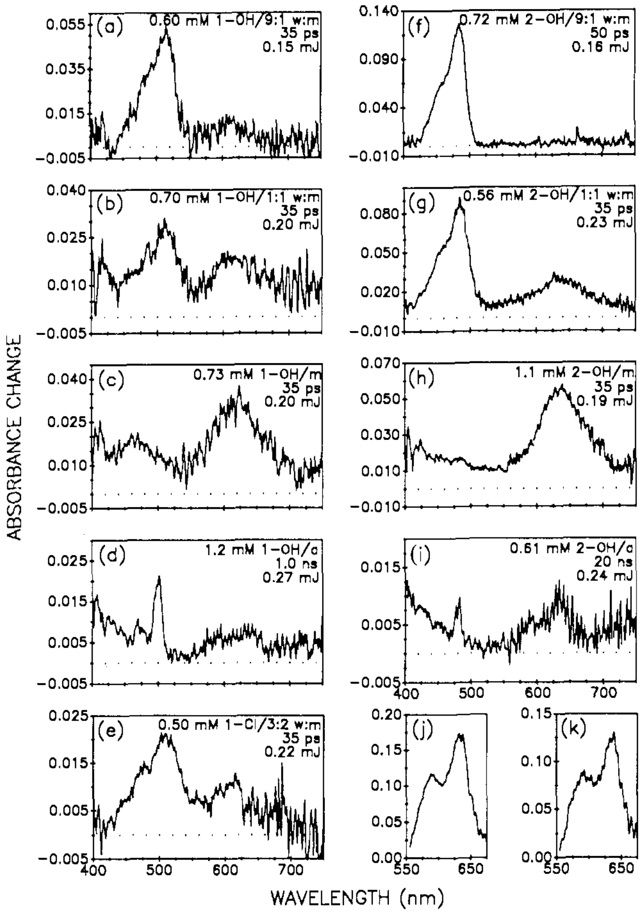

**Figure 1.** Transient absorption spectra recorded at the listed times after 266- (a–i) or 355-nm (j,k), 30-ps excitation of the indicated samples; w = $H_2O$, m = $CH_3OH$, a = $CH_3CN$; for (j), 50 mM **1**-OH and 20 mM **3** in $CH_3CN$, 20 ns, 0.24 mJ; for (k), 50 mM **2**-OH and 20 mM **3** in $CH_3CN$, 20 ns, 0.22 mJ. Each spectrum is the average of ~400 spectra. The indicated average excitation pulse energies are within the range for which the spectral intensity changes linearly as a function of pulse energy. Samples were not significantly changed via photochemical or thermal reaction during the time required for the laser spectroscopic measurements.

Series of difference absorption spectra recorded after 266-nm, 30-ps excitation of **2**-OH parallel those recorded for **1**-OH in the corresponding solvent and provide further support for the assignment of the $\mathbf{1}^+$ absorption band. In 9:1 $H_2O/CH_3OH$, only a promptly appearing 485-nm absorption band ($\tau_d = 275 \pm 20$ ps) is observed (Figure 1f). In 1:1 $H_2O/CH_3OH$, two bands, a stronger one ($\lambda_{max} = 485$ nm; $\tau_d = 75 \pm 15$ ps) and a weaker one ($\lambda_{max} \simeq 635$ nm; $\tau_d < 20$ ps), appear promptly (Figure 1g). Excitation of **2**-OH in $CH_3OH$ or $CH_3CN$ results in the prompt appearance of a broad absorption band ($\lambda_{max} = 645$ nm) throughout the region of interrogation (Figure 1h) which decays

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[8] Promptly after 266-nm excitation of **1**-$OCH_3$ in $CH_3CN$ or 1:1 $H_2O/CH_3OH$, similar absorption assigned to transitions from $S_1$ of **1**-$OCH_3$ is observed.

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to ~10% of its maximum intensity by 1.0 ns after excitation. In $CH_3CN$, a weak absorption band at 480 nm, which is assigned to $2^{\bullet}$,[9] and an absorption which extends from <400 nm are apparent at longer times when the promptly appearing absorption has decayed substantially (Figure 1i).

The 485-nm band shown in Figure 1 (parts f and g) agrees well with the sole band at 488 nm which was reported and assigned by Deno et al.[4a] to $\mathbf{2}^+$ generated from **2**-OH in sulfuric acid. We assign the longer wavelength absorption band ($\lambda_{max} \simeq 635$ nm) in Figure 1g to an $S_n \leftarrow S_1$ transition of **2**-OH. The shorter wavelength $\lambda_{max}$ of $\mathbf{2}^+$ relative to $\mathbf{1}^+$ is consistent with the ground-state spectra of other 1,1-diarylethyl cations relative to the corresponding diarylmethyl cation.[4a,11] The intensities and decay kinetics of this 485-nm band in the several solvents relative to the 515-nm band observed after excitation of **1**-OH are consistent with the generation of $\mathbf{2}^+$ and the more reactive $\mathbf{1}^+$.[12,14] In view of the recent interest in the enhanced reactivities of electronically excited precursors to give cyclic $4n$ $\pi$-electron systems relative to $(4n + 2)$ $\pi$-electron analogues,[5,10,16] our spectroscopic studies do not provide any evidence for the intermediacy of excited-state $\mathbf{1}^+$ or $\mathbf{2}^+$.

It was suggested[4b] that, under the conditions of Deno et al.,[4a] the cation radical of **1**-OH may have been generated. The following data support this suggestion. We observed that 355-nm excitation of chloranil (**3**) in $CH_3CN$ in the presence of 50 mM **1**-OH gives rise to the generation of $\mathbf{3}^{\bullet -}$ ($\lambda_{max} = 450$ nm)[17] and an absorption band ($\lambda_{max} = 635$, ~590 nm; Figure 1j) that appears on the time scale of the conversion of $^3\mathbf{3}^*$ to $\mathbf{3}^{\bullet -}$. This band, which we assign to **1**-$OH^{\bullet +}$, exhibits a $\lambda_{max}$ near the longer wavelength band reported and assigned by Deno et al.[4a] to $\mathbf{1}^+$. When **3** is excited in the presence of **2**-OH in $CH_3CN$, an absorption band ($\lambda_{max} = 640$, ~590 nm; Figure 1k), which we assign to **2**-$OH^{\bullet +}$, is observed.[18]

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(14) After we submitted this communication for publication, we received two preprints[15,16] of papers describing studies of photosolvolyses of **1**-OH. We thank Professors M. A. Fox and P. Wan for copies of these preprints. An absorption band at 640 nm was assigned[15] to $\mathbf{1}^+$ (in 9:1 $H_2O/CH_3OH$, $\tau_d$ = 6.25 μs). This assignment and lifetime do not agree with our results for $\mathbf{1}^+$. The relatively long 6.25-μs lifetime[15] does not appear to be consistent with the results of attempted trapping[16] of $\mathbf{1}^+$. The 640-nm absorption bands reported[15] for flash photolysis of **1**-OH and for pulse radiolysis of **1**-Cl agree well with those that we report herein for cation radicals of substituted fluorenes. Unlike the (5.3 ± 0.5)-ns fluorescence lifetime observed[15] for **1**-OH in 9:1 $H_2O/CH_3OH$, the fluorescence lifetimes of **1**-OH and **2**-OH reported[16] to be ~0.3 ns in $CH_3CN$ and estimated[16] to be ~30 ps in 4:1 $H_2O/CH_3CN$ are consistent with our time-resolved absorption data.

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# Enantiospecific Total Synthesis of Pseudopterosins A and E

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Although there has been an explosive growth in the number and variety of naturally occurring compounds identified from marine organisms in recent years, very few have shown therapeutically significant biological activity. A striking exception appears to be the case of the pseudopterosins, isolated from the sea plume *Pseudopterogorgia elizabethae*,[1,2] which have powerful antiinflammatory activity and which are not prostaglandin $H_2$ synthase inhibitors.[2] Most noteworthy with respect to biological activity are pseudopterosin A (**1**) and pseudopterosin E (**2**), the latter by far the most active known member of this series.[1d,3] In this communication we describe a useful route to **1** and **2** via the corresponding aglycone and new methodology for aromatic annulation, selective elaboration of catechols, and α-fucosylation.

The oxime **3**, readily available from (1*S*,2*R*,5*S*)-(+)-menthol nitrite ester by photolysis as a 5:1 mixture of *R* and *S* diastereomers at C(8),[4,5] was converted to a single γ-lactone (**4**), mp 35-36 °C (60% overall), by the following sequence: (1) oxime hydrolysis with 5 equiv of aqueous $NaHSO_3$[6] at 50 °C for 4 h; (2) lactol → lactone oxidation ($Br_2$ in $THF-H_2O-CaCO_3$ at 23 °C for 1.5 h); and (3) complete isomerization at C(8) to the *R* configuration (lithium diisopropylamide (LDA) in THF at 0 °C for 2 h, followed by quenching at 0 °C with aqueous $NH_4Cl$). The octalone **5** was synthesized from **4** in 40% overall yield by the following sequence: (1) reduction of **4** to the corresponding lactol with diisobutylaluminum hydride in $CH_2Cl_2$ at -78 °C for 2 h; (2) Wittig chain extension with $Ph_3P{=}C(CH_3)SEt$[7] in DMSO at 23 °C for 24 h; (3) Swern oxidation[8] with DMSO, $(CF_3CO)_2O$, and $Et_3N$ in $CH_2Cl_2$ at -65 °C for 1 h; (4) thioether cleavage ($HgCl_2$, in $CH_3CN-H_2O$ at 50 °C for 1 h);[9] and (5) aldol cyclization of the resulting 1,5-diketone with $NaOCH_3$ in $CH_3OH$ at 23 °C for 12 h to give **5**.

Reaction of enone **5** with KH in THF-HMPA at 23 °C for 12 h followed by treatment with *tert*-butyldimethylsilyl chloride afforded the enol ether **6** (97%) which was transformed into diketone **7** in two steps (61% overall): (1) slow addition of **6** in $CH_2Cl_2$ (over 2 h) to a solution of 2-butynal and trimethylsilyl triflate in $CH_2Cl_2$ at -78 °C and quenching with water after an additional hour;[10] and (2) oxidation of the resulting propargylic alcohol by pyridinium chlorochromate in $CH_2Cl_2$ at 23 °C for 3 h in the presence of 4A molecular sieves. The tricyclic nucleus of the pseudopterosins was then constructed by a new aromatic annulation procedure which is related to a cyclization previously

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