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Excited-State Dynamics of 1-Piperidino- or 1-Pyrrolidino-anthraquinone for Formation of *N*−Ylide and Reduced Compounds

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By means of subpicosecond laser photolysis of the title compound at room temperature, time-dependent shift of an absorption band has been observed at short delay times which is ascribed to solvent reorganization around the lowest excited singlet state of the solute molecule with an intramolecular charge-transfer character. In comparison with the results obtained by nanosecond laser photolysis and steady-state photolysis at 77 K, it is concluded that the lowest excited singlet state undergoes rapid intramolecular proton transfer forming an *N*-ylide compound. For formation of the *N*-ylide compound from the lowest excited singlet state of 1-piperidino-anthraquinone, it is considered that there exists an intermediate which can be ascribed to transfer of the equatorial proton to the carbonyl oxygen anion. At room temperature, no formation of *N*-ylide compound as a stable compound can be observed due to its rapid reversion to 1-piperidino- or 1-pyrrolidino-anthraquinone. Steady-state photolysis in ethanol at room temperature gives rise to formation of a reduced compound. Yield of the reduced compound is obtained by 405 or ≥510 nm photolysis, however, is negligibly small compared with that obtained by 313 or 366 nm photolysis. Hence, it is proposed that intersystem crossing from a higher excited singlet state (probably the second excited singlet state) to a higher excited triplet state (probably the third excited triplet state) followed by internal conversion to the lowest excited triplet (T_1) state plays an important role for the photoreduction, i.e., the reduced compound may be formed from the T_1 state, although the possibility of additional photoreduction originating from the second excited triplet state cannot be ruled out.

Introduction

In connection with the interest in the excited-state behavior of substituted anthraquinones, we studied photoinduced intramolecular hydrogen-atom transfer of 1,4-hexyl-bridged anthraquinone[1] as well as 1-methyl- and 1,4-dimethylanthraquinones.[2] Although both their lowest excited singlet and triplet states gave rise to generation of the corresponding excited biradicals, the final products were as follows. (1) For sterically strained 1,4-hexyl-bridged anthraquinone with a boat-formed deformation benzene ring, the ground-state singlet biradical and its methide (1,4-hexylidene-bridged 9-hydroxyanthracene-10-one) were formed in equilibrium. Although these products were stable at 77−140 K, they (or one of them) produced at room temperature changed to 1,4-hexylidene-bridged anthraquinone (product **1**) in aprotic solvents [or to product **1** (minor) and 1,4-hexyl-bridged 1,4-diethoxy-9,10-dihydroxyanthracene (product **2**, major) in ethanol and a mixed solvent (EPA) of diethyl ether/isopentane/ethanol = 5:5:2 in volume ratio] (cf., Scheme 1); also interconversion of products $\mathbf{1} \rightleftharpoons \mathbf{2}$ by the change of an aprotic solvent $\rightleftharpoons$ ethanol (or EPA) and slow thermal reversion of products **1** and **2** to the original anthraquinone could be seen at room temperature.

(2) For planar 1-methyl- or 1,4-dimethylanthraquinone, however, 9-hydroxy-1,10- or 9-hydroxy-4-methyl-1,10-anthraquinone-1-methide was formed, respectively; these methides were stable at 77 K but rapidly reverted to the original anthraquinones at room temperature. An additional interesting photochemistry of 1,4-dimethylanthraquinone in ethanol at room temperature was formation of 1,4-dimethyl-9,10-dihydroxyanthracene from not the lowest excited triplet state but the third excited singlet or triplet state, i.e., this higher excited singlet or triplet state abstracted a hydrogen atom from the solvent generating the semiquinone radical as the intermediate for formation of 1,4-dimethyl-9,10-dihydroxyanthracene. In accordance with photoreduction of anthraquinone or its haloderivatives (the chloro and bromo compounds),[3,4] however, formation of 1-methyl-9,10-dihydroxyanthracene from 1-methylanthraquinone was ascribed to hydrogen-atom abstraction from ethanol by the lowest excited triplet state.

By measurements of the absorption spectra of anthraquinones (anthraquinone and its halo or alkyl derivatives), one can easily find out that their lowest excited singlet states are of a typical nπ^* character. In contrast, the absorption spectra of 1-piperidino (PIAQ) and 1-pyrrodino (PYAQ) anthraquinones shown in Figure 1 later indicate that their lowest excited singlet (S_1) and thus triplet (T_1) states are of a charge-transfer character. As an extension of our studies on the photophysics and photochemistry of aromatic carbonyl compounds with S_1 and T_1 states of no charge-transfer character,[1−12] therefore, the present paper deals with the excited-state dynamics of PXAQ (PIAQ or PYAQ) for formation of *N*-ylide and reduced compounds. The former product is formed from the S_1 state, while the latter product may be formed from the T_1 state, although the possibility of additional photoreduction originating from the second excited triplet state cannot be ruled out.

Experimental Section

Following the method reported by Inoue et al.,[13] PXAQ was synthesized by a reaction of 1-chloroanthraquinone and piperidine for PIAQ (or pyrrolidine for PYAQ) and then purified; all

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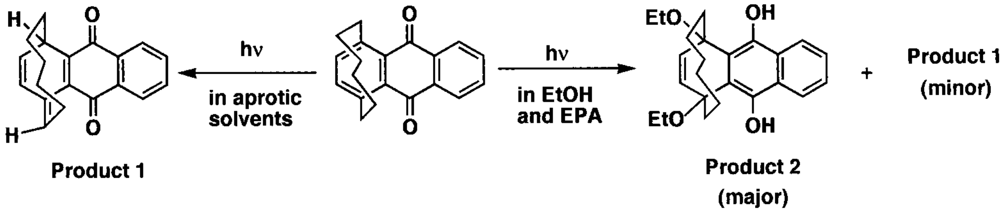


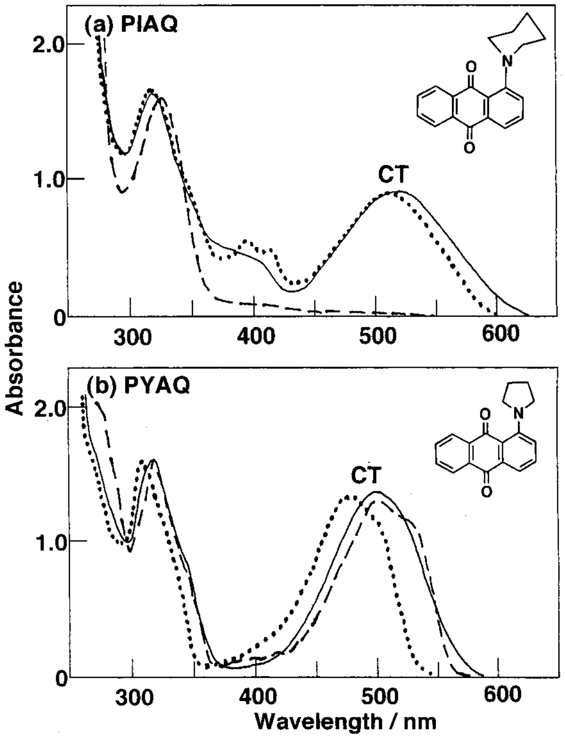
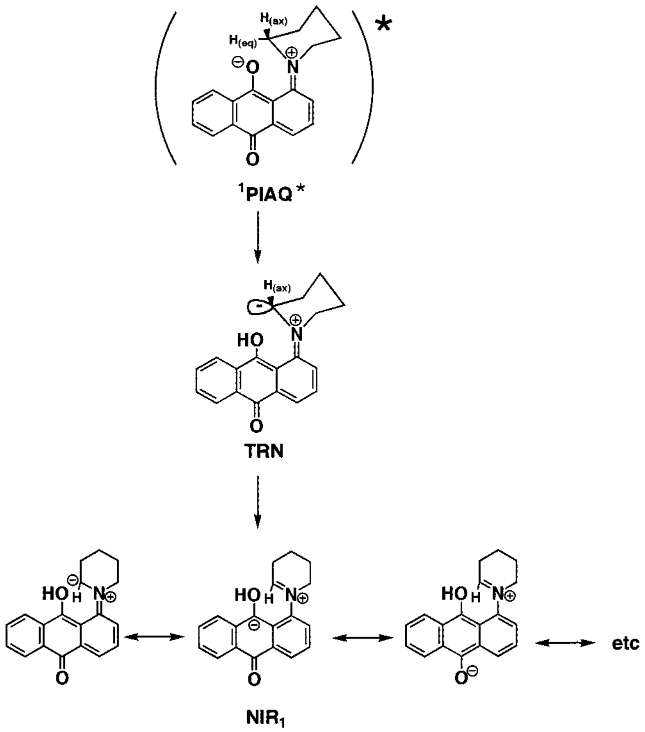


Figure 1. Absorption spectra of PXAQ recorded in ethanol (—) and cyclohexane (···) at room temperature. The dashed line in (a) is the absorption spectrum of anthraquinone recorded in ethanol at room temperature, while that in (b) is the absorption spectrum of PYAQ recorded in EPA at 77 K.

these EP-grade reactants were purchased from Wako. The solvents used were cyclohexane, ethanol, and EPA. Although Uvasol diethyl ether (Merck) and spectral-grade cyclohexane (Dojin) were used without further purification, GR-grade isopentane (Wako) was purified by passing it through an alumina column and spectral-grade ethanol (Nacalai) was dried using a molecular sieve 3A (Wako). The sample solutions used for subpicosecond laser photolysis in a flow cell of 2 mm path length were deoxygenated by bubbling of Ar gas, while those used for nanosecond laser photolysis and steady-state photolysis in a cell of 10 mm path length were degassed by several freeze−pump−thaw cycles.

Subpicosecond laser photolysis was performed by a pump−probe method using a laser photolysis system comprising a femtosecond mode-locked Ti:sapphire oscillator (Tsunami, model 3960) and a regenerative amplifier (model TSA-50) from Spectra-Physics;[14] both intensities of the excitation light pulse [the second (400 nm) or third (267 nm) harmonic] and the probing light pulse (the white-light continuum generated by focusing the 800 nm fundamental into water) were approximated by a Gaussian function with a full width at the half-maximum intensity (fwhm) of 0.25 ps. For nano-second sample excitation, the third harmonic (355 nm, fwhm = 5 ns) from a Nd^{3+}:YAG laser (Continuum Surelight I) was used and the transient absorption spectra were recorded using a multichannel analyzer.[15]

SCHEME 2



Steady-state photolysis was carried out using the 313, 366, 405, or ≥510 nm monochromatic light selected from a USH-500D super-high-pressure mercury lamp, and the resulting absorption spectral changes were recorded using a Hitachi 200−20 spectrophotometer.

Results and Discussion

Solvent Reorganization around the Lowest Excited Singlet State of PXAQ (PIAQ or PYAQ). Although Inoue et al.[16] reported that PIAQ was weakly fluorescent, we have observed no genuine fluorescence and phosphorescence attributable to PXAQ (PIAQ or PYAQ); measurements of the emission excitation spectrum, however, reveal the existence of a fluorescent byproduct. As shown in Figure 1, the absorption spectrum of PXAQ recorded in ethanol (the solid line) or cyclohexane (the dotted line) at room temperature has the longest-wavelength absorption band (CT). No such a broad band can be seen for anthraquinone or its haloderivative (the chloro or bromo compound) with the lowest excited singlet (S_1) state of a typical $n\pi^*$ character;[4,7] as a typical example, an absorption spectrum (the dashed line) of anthraquinone in ethanol at room temperature is also shown in Figure 1a. Hence, band CT observed for PXAQ can be assigned to the absorption corresponding to transition from the almost neutral ground state to the S_1 state (^{1}PXAQ* = ^{1}PIAQ* or ^{1}PYAQ*) of a charge-transfer character (cf., Scheme 2 or 3).[13,18−20] In fact, an absorption maximum of band CT at the wavelength of λ_{max} shifts

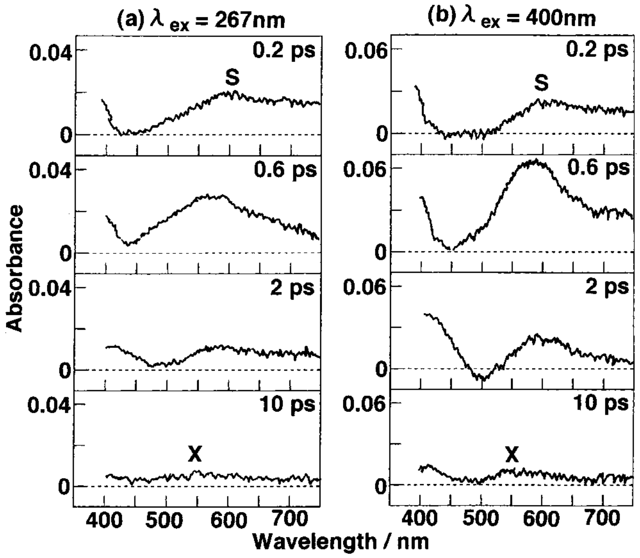


Figure 2. Transient absorption spectra obtained by subpicosecond laser photolysis of PIAQ in ethanol at room temperature. λ_{ex} are the excitation wavelengths.

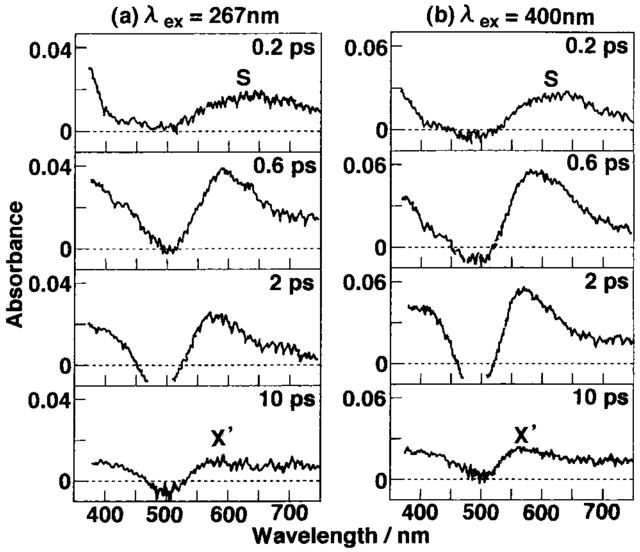


Figure 3. Transient absorption spectra obtained by subpicosecond laser photolysis of PYAQ in ethanol at room temperature. λ_{ex} are the excitation wavelengths.

with the change of the dielectric constant (ϵ)[17] of a solvent as follows: λ_{max} = 498, 502, 512, 512, 513, 515, or 513 nm for PIAQ, or λ_{max} = 475, 479, 493, 495, 500, 500, or 496 nm for PYAQ in 3-methylpentane ($\epsilon = 1.895$), cyclohexane ($\epsilon = 2.220$), benzene ($\epsilon = 2.275$), acetone ($\epsilon = 20.70$), ethanol ($\epsilon = 24.55$), methanol ($\epsilon = 32.70$), or acetonitrile ($\epsilon = 37.5$), respectively.

At room temperature, 267 or 400 nm subpicosecond laser photolysis of PXAQ in ethanol gives rise to the appearance of transient absorption spectra shown in Figures2 and 3. Irrespective of the excitation wavelength (λ_{ex}), band S at short delay times shifts with time to a shorter wavelength and after then no such a shift can be seen. Similar results are obtained in cyclohexane. Owing to the broad width of band S, however, Figure 4 indicates that the absorbance of band S monitored at a given wavelength (λ_{mo}) builds up within a duration of pulse excitation and then decreases with time to a constant absorbance following a single-exponential function. Since the lifetime (τ_s = 0.5−2.0 ps) of band S thus obtained is independent of λ_{ex}, we believe that band S is due to the absorption of ^{1}PXAQ* and the results shown in Figures 2 and 3 can be interpreted in terms of the single-exponential decay of ^{1}PXAQ* accompanied by generation of another transient species. In fact, the transient absorption spectra (with band X or X′) obtained at 10 ps delay are somewhat different from those (with band S) obtained at shorter delay times.

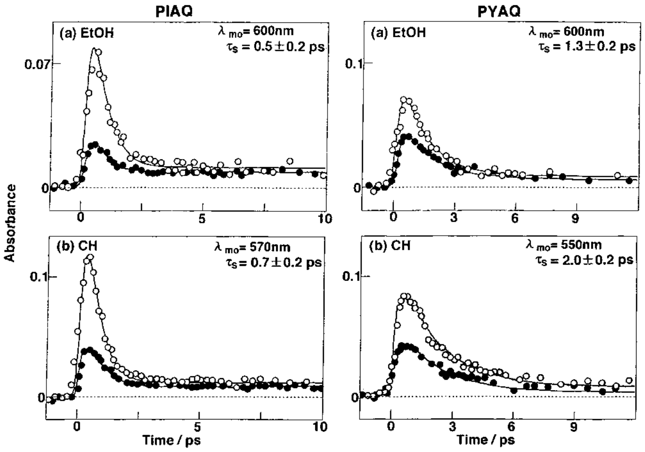


Figure 4. Absorbance changes of band S with time obtained by 267 (●) or 400 (○) nm subpicosecond laser photolysis of PXAQ in (a) ethanol or (b) cyclohexane at room temperature. λ_{mo} are the monitoring wavelengths and the solid curves are best-fit ones calculated by the single-exponential function with a lifetime of τ_s.

To find out the detail of time-dependent spectral shift observed for band S at short delay times, the wavenumbers (v_t) of band maxima are plotted against the delay time (t) and the results obtained by 267 nm excitation of PXAQ in ethanol (open circles) and cyclohexane (closed circles) are shown in Figure 5, where the solid curves are the best-fit functions given by eq 1 with $f_i (i = 1, 2) > 0$ and $\sum f_i = 1$; t_0 and t_∞ are the delay times indicated, and τ_i (i = 1, 2) are the time constants for the tentatively assumed biexponential band shift.

$$v_t = v_\infty - (v_\infty - v_t)\sum f_i \exp(-t/\tau_i)/\sum f_i \exp[-t_0/\tau_i] \quad (1)$$

By 400 nm excitation, similar results are obtained and all biexponential fit parameters ($\tau_{1,2}$ and $f_{1,2}$) obtained so far as well as two mean times [$<\tau_a> = 1/\sum(f_i/\tau_i)$ and $<\tau_b> = \sum f_i\tau_i$] thus calculated are listed in Table 1. Interestingly, $\tau_{1,2}$ are independent of the excitation wavelength and the values obtained for PIAQ are equal to those obtained for PYAQ; for $<\tau_{a,b}>$, however, there is a small change by the change of the excitation wavelength or the solute molecule. Since the changes of $\tau_{1,2}$ and $<\tau_{a,b}>$ by the change of solvent are significant and excitation of PXAQ using the depolarized light pulse gives the identical results, time-dependent shift of band S shown in Figure 2 or 3 may reflect solvent reorganization around ^{1}PXAQ*. As shown in Figure 1, a weak absorption band around 400 nm is clearly seen only for PIAQ at room temperature but the existence of this band for PYAQ is supported by its absorption spectrum (the dashed line shown in Figure 1b) recorded in EPA at 77 K. It thus can be concluded that 267 or 400 nm excitation of almost neutral PXAQ populates ^{1}PXAQ* of a charge-transfer character via rapid internal conversion from a higher excited singlet state-(s): ^{1}PXAQ* is expected to have a charge-transfer character smaller than the lowest excited singlet of 2-piperidino or 2-pyrrolidino-anthraquinone, but the time constants $\tau_{1,2}$ obtained for the 2-substituted compounds are found to be identical with those obtained for ^{1}PXAQ*;[21] owing to the change of $f_{1,2}$, however, the meantimes are somewhat different, i.e., $<\tau_a> =$

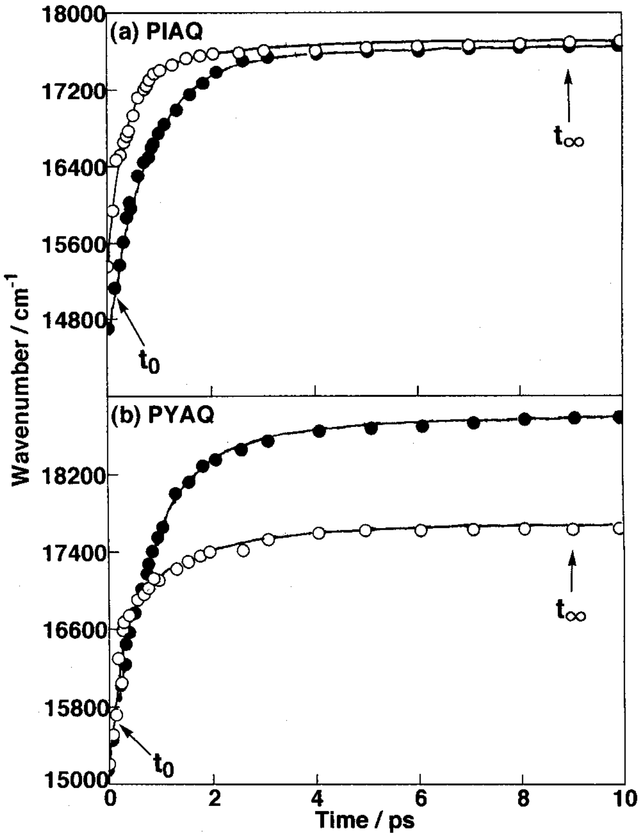


Figure 5. Plots of wavenumbers (ν_t) at the absorption maxima of band S against the delay time (t) obtained by 267 nm subpicosecond laser photolysis of PXAQ in ethanol (○) or cyclohexane (●) at room temperature. The smooth curves are the best-fit biexponential functions given by eq 1 with time costants τ_1 and τ_2 listed in Table 1.

0.42−0.50 ps and $\langle\tau_b\rangle$ = 0.74−0.95 ps in ethanol (or $\langle\tau_a\rangle$ = 0.70−0.80 ps and $\langle\tau_b\rangle$ = 0.82−1.11 ps in cyclohexane).

Meanwhile, Horng et al.[22] performed measurements of the time-resolved fluorescence spectra of coumarin 153 (C153) in various solvents and analyzed time-dependent spectral shift by a multiexponential form of eq 1. For example, τ_i and f_i obtained for ethanol were as follows; $\tau_1 = 0.030$ ps ($f_1 = 0.085$), $\tau_2 = 0.39$ ps ($f_2 = 0.230$), $\tau_3 = 5.03$ ps ($f_3 = 0.182$), and $\tau_4 = 29.6$ ps ($f_4 = 0.502$) giving $\langle\tau_a\rangle = 0.29$ ps and $\langle\tau_b\rangle = 16$ ps. The temporal resolution of our laser photolysis system, however, is 0.25 ps and no time constant longer than 1.66 ps can be seen for ethanol owing to a short lifetime (τ_s = 0.5 or 1.3 ps) of ^{1}PXAQ*. Ignoring the shortest (τ_1 and f_1) and longest (τ_4 and f_4) components stated above, therefore, $\langle\tau'_a\rangle = [f_2/(f_2 + f_3)\tau_2 + f_3/(f_2 + f_3)\tau_3]^{-1} = 0.66$ ps and $\langle\tau'_b\rangle = f_2\tau_2/(f_2 + f_3) + f_3\tau_3/(f_2 + f_3) = 2.44$ ps are obtained. Clearly, the former mean time is roughly comparable with $\langle\tau_a\rangle$ = 0.35−0.41 ps but the latter mean time is greatly different from $\langle\tau_b\rangle$ = 0.50−0.72 ps (cf., Table 1). For the time-resolved fluorescence spectra of C135 in cyclohexane, Horng et al.[22] anticipated no spectral relaxation reflecting solvent reorganization around the excited solute molecule but its dynamics was ascribed to the vibrational relaxation. For solvation due to benzene, however, they obtained the following values; $\tau_1 = 0.234$ ps ($f_1 = 0.366$), $\tau_2 = 1.89$ ps ($f_2 = 0.600$), and $\tau_3 = 24.7$ ps ($f_3 = 0.034$). Ignoring the lowest components (τ_3 and f_3), one can get $\langle\tau'_a\rangle = [f_1/(f_1 + f_2)\tau_1 + f_2/(f_1 + f_2)\tau_2]^{-1} = 0.51$ ps and $\langle\tau'_b\rangle = f_1\tau_1/(f_1 + f_2) + f_2\tau_2/(f_1 + f_2) = 1.26$ ps. Again, only the former mean time is comparable with $\langle\tau_a\rangle$ = 0.61−0.74 ps obtained by us for cyclohexane using the probe molecule (^{1}PXAQ*) with a lifetime of 1.0 or 2.5 ps. The dielectric constant ($\epsilon = 2.27$) and the refractive index ($n = 1.50$) of benzene are nearly equal to those ($\epsilon = 2.02$ and $n = 1.42$) of cyclohexane.[17] Also, the reaction field factor $[F(\epsilon, n) = (\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)]$[23−26] calculated for benzene (0.01) is nearly equal to that calculated for cyclohexane (0.00). Hence, a comparison of $\langle\tau'_a\rangle = 0.51$ ps obtained for benzene by Horng et al.[22] with $\langle\tau_a\rangle$ = 0.61−0.74 ps obtained for cyclohexane by us might be reasonable.[27] We thus prefer $\langle\tau_a\rangle$ listed in Table 1 as the characteristic mean time for solvent reorganization around a very short-lived excited solute molecule such as ^{1}PXAQ*.

Photoinduced Intramolecular Proton Transfer of PXAQ (PIAQ or PYAQ) Yielding an *N*−Ylide Compound. For PIAQ in EPA, 355 nm nanosecond laser photolysis at room temperature gives rise to the appearance of no transient absorption spectrum but that at 77 K reveals the existence of two absorption bands shown in Figure 6a−c. Clearly, band A obtained at the end of pulse excitation (10 ns delay) is somewhat different from band B obtained at 1 μs or 1 ms delay and no decay of band B with time can be seen. Owing to the weak absorption and its small change with time, the decay curve of band A cannot be measured but the time constant for A → B band shift is found to be less than 50 ns. For comparison, the normalized absorption spectrum (with band X) obtained by subpicosecond laser photolysis of PIAQ in ethanol at room temperature is shown by the dotted line in Figure 6a. Since this spectrum is rather similar to that with band A, it is reasonable that band S responsible for ^{1}PIAQ* changes to band X = A responsible for a transient species (TRN) which is an intermediate for formation of a product (PI-77 with band B) stable at 77 K. For PYAQ in EPA, nanosecond laser photolysis at room temperature also gives rise to no appearance of a transient absorption spectrum, but that at 77 K reveals the existence of only one absorption band (C) which exhibits no time-dependent shift and disappears at 5 ms delay (cf., Figure 6d−f). Band C is similar to the normalized absorption spectrum (the dotted line with band X′) obtained by subpicosecond laser photolysis of PYAQ in ethanol at room temperature. On the basis of the discussion stated later, we believe that band X′ = C is the absorption of a product (PY-77) which is unstable even at 77 K and formed from ^{1}PYAQ* via no intermediate.

No observation of bands A and B for PIAQ (or band C for PYAQ) by nanosecond laser photolysis at room temperature may reflect very rapid TRN → PI-77 → PIAQ or PY-77 → PYAQ reversion. In fact, steady-state photolysis of PXAQ at room temperature reveals no formation of PI-77 or PY-77. At 77 K in EPA, steady-state photolysis of PYAQ also reveals no reaction but that of PIAQ causes the absorption spectral change which is independent of the excitation wavelength as shown in Figure 7, i.e., with the decrease of band R_2, band R_1 increases and two new bands ($P_{1,2}$) grow in. Since band B shown in Figure 6b or 6c does not decrease with time, we believe that this band is identical with band P_2; owing to the superposition of reactant and product absorptions (bands R_3 and P_2, respectively), however, band P_2 looks as if it is shifted to a shorter wavelength compared with band B. After photolysis, warming of the sample up to room temperature causes the disappearance of bands $P_{1,2}$ accompanied by the decrease and increase of bands R_1 and R_2, respectively. The absorption spectrum recorded after re-cooling of the sample down to 77 K is confirmed to be absolutely identical with that of the original compound (PIAQ) in regard to the spectral profile and intensity. This indicates that the photoproduct (PI-77) formed at 77 K reverts quantitatively to PIAQ at a higher temperature than 77 K.

TABLE 1: Biexponential Fit Paramrters ($\tau_{1,2}$, $f_{1,2}$) and Mean Time Constants ($<\tau_{a,b}>$) for Time-Dependent Shift of Band S Observed by 267 nm Subpicosecond Laser Photolysis of PXAQ in Ethanol (EtOH) and Cyclohexane (CH) at Room Temperature[a]

	PIAQ				PYAQ			
solvent	τ_1/ps	f_1	τ_2/ps	f_2	τ_1/ps	f_1	τ_2/ps	f_2
EtOH	0.31 ± 0.03	0.80 ± 0.03	1.66 ± 0.14	0.20 ± 0.03	0.31 ± 0.03	0.70 ± 0.03	1.66 ± 0.14	0.30 ± 0.03
	(0.31 ± 0.04	0.75 ± 0.03	1.66 ± 0.14	0.25 ± 0.03	0.31 ± 0.02	0.86 ± 0.02	1.66 ± 0.14	0.14 ± 0.02)
	$<\tau_a> = 0.37$ ps	(0.39 ps),	$<\tau_b> = 0.58$ ps	(0.65 ps)	$<\tau_a> = 0.41$ ps	(0.35 ps),	$<\tau_b> = 0.72$ ps	(0.50 ps)
CH	0.65 ± 0.05	0.88 ± 0.03	2.50 ± 0.40	0.12 ± 0.03	0.65 ± 0.05	0.83 ± 0.02	2.50 ± 0.30	0.17 ± 0.02
	(0.65 ± 0.04	0.92 ± 0.03	2.50 ± 0.50	0.08 ± 0.03	0.65 ± 0.04	0.92 ± 0.02	2.50 ± 0.50	0.08 ± 0.02)
	$<\tau_a> = 0.71$ ps	(0.61 ps),	$<\tau_b> = 0.89$ ps	(0.80 ps)	$<\tau_a> = 0.74$ ps	(0.69 ps),	$<\tau_b> = 0.96$ ps	(0.80 ps)

[a] The values in parentheses are obtained by 400 nm subpicosecond laser photolysis.

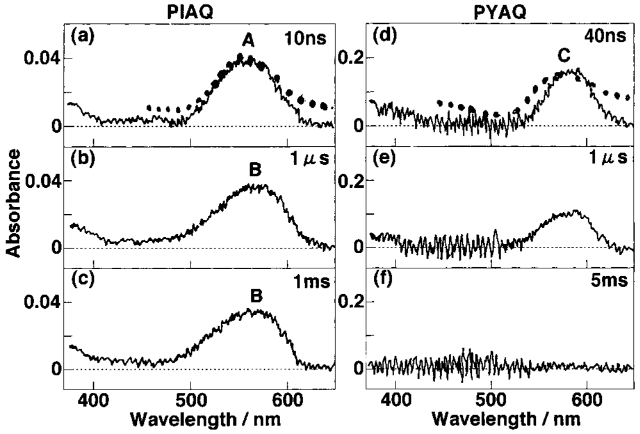


Figure 6. Transient absorption spectra (—) obtained by 355 nm nanosecond laser photolysis of (a−c) PIAQ and (d−f) PYAQ in EPA at 77 K. The dotted lines are the normalized absorption spectra obtained by subpicosecond laser photolysis of PXAQ in ethanol at room temperature, where the delay time is 10 ps.

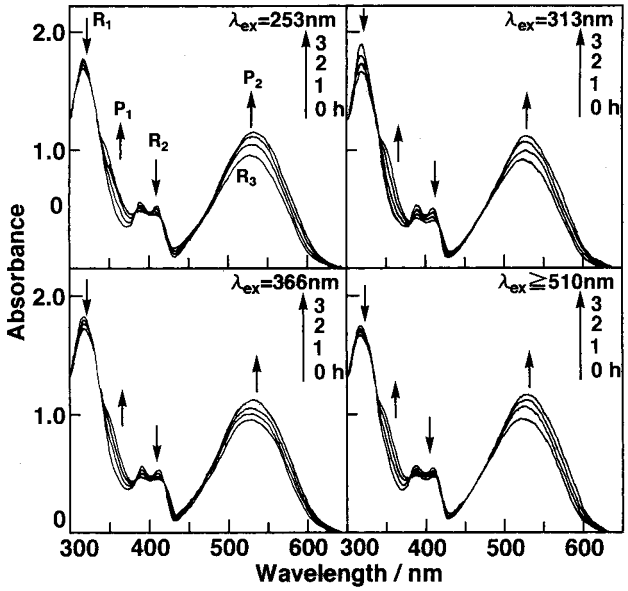


Figure 7. Absorption spectral change caused by steady-state photolysis of PIAQ in EPA at 77 K. λ_{ex} are the excitation wavelengths.

Upon steady-state photolysis, the spectral profiles of bands $P_{1,2}$ observed at 77 K and their disappearance accompanied by the appearance of absorption bands due to only the original compound (PIAQ) by elevation of temperature up to room temperature are very similar to those observed for the absorption bands of several methides formed from alkylanthraquinones;[2,28] band P_2 is also similar to the absorption bands of the ground-state biradical and its methide formed in equilibrium from sterically strained 1,4-hexyl-bridged anthraquinone,[1] but these products (or one of them) changed to another solvent-dependent product(s) at room temperature (cf., Scheme 1). By subpicosecond (or picosecond) and nanosecond laser photolysis of alkylanthraquinones[2] (or 1,4-hexyl-bridged anthraquinone[1]), it was found that both their lowest excited singlet and triplet states underwent intramolecular hydrogen-atom transfer generating the corresponding excited biradicals as the intermediates for formation of the methides from alkylanthraquinones (or formation of the ground-state biradical and its methide from 1,4-hexyl-bridged anthraquinone). For PIAQ, however, no transient absorptions reflecting generation of an excited triplet species (or formation of PI-77 from the lowest excited triplet state) can be seen. As shown in Scheme 2, we thus believe that ^{1}PIAQ* undergoes intramolecular proton-transfer generating TRN as an intermediate for formation of PI-77 which may be an *N*-ylide compound (NIR_1),[29] i.e., band X = A and B=P_2 are due to the absorption of TRN and NIR_1, respectively;[30] since two hydrogen atoms at the 2′-methylene group of PIAQ are axial and equatorial, generation of TRN from ^{1}PIAQ* by transfer of the equatorial proton to the carbonyl oxygen anion is reasonable.

As stated previously, no product formation can be seen by steady-state photolysis of PYAQ in EPA at 77 K. On the basis of the results obtained by subpicosecond laser photolysis at room temperature and nanosecond laser photolysis at 77 K, however, we believe that ^{1}PYAQ* of a charge-transfer character also undergoes intramolecular proton transfer from the 2′-methylene group to the carbonyl oxygen anion forming an *N*-ylide compound (NIR_2) responsible for band X = C. In comparison with the resonance structures of NIR_1 formed from ^{1}PIAQ* (cf. Scheme 2), those of NIR_2 formed from ^{1}PYAQ* (cf. Scheme 3) have a five-membered ring and thus may be unstable resulting in no existence of stable NIR_2 even at 77 K. At the 2′-methylene group of PYAQ, furthermore, neither the axial nor equatorial hydrogen atom can exist and two hydrogen atoms are almost equivalent. This suggests that NIR_2 may be formed from ^{1}PYAQ* via no such an intermediate as observed for formation of NIR_1 from ^{1}PIAQ*.

Photoinduced Intermolecular Hydrogen-Atom Abstraction of PXAQ (PIAQ or PYAQ) Yielding a Reduced Compound. As shown by the solid lines in Figure 8a or 8c, 313 nm steady-state photolysis of PXAQ (PIAQ or PYAQ) in ethanol at room temperature causes an absorption spectral change different from that observed for PIAQ in EPA at 77 K (cf., Figure 7). Clearly, the decrement of reactant absorption bands upon photolysis is accompanied by the increment of a product absorption band which is different from those of $NIR_{1,2}$. After photolysis, furthermore, introduction of air causes quantitative conversion of the photoproduct back to the original compound (cf., the dashed spectrum shown in Figure 8a or 8c). The product absorption band and its disappearance by introduction of air observed for PXAQ are very similar to those observed for the reduced compounds (9,10-dihydroxyanthracenes) formed

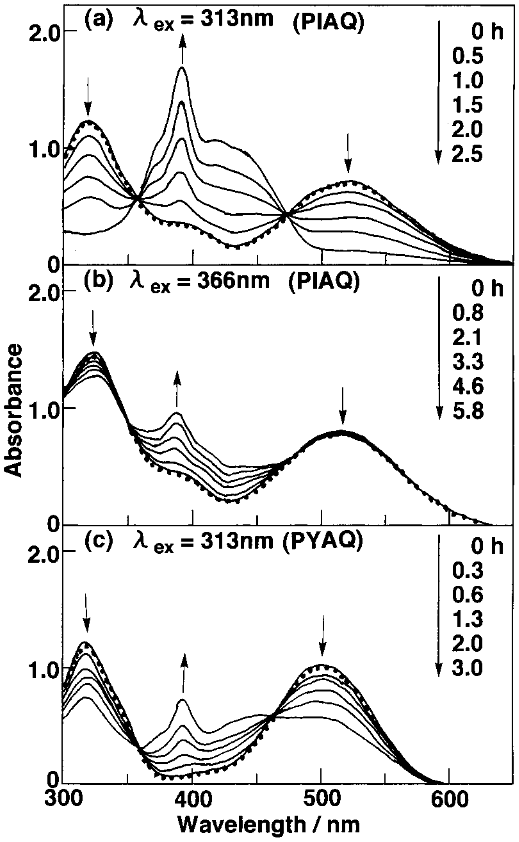
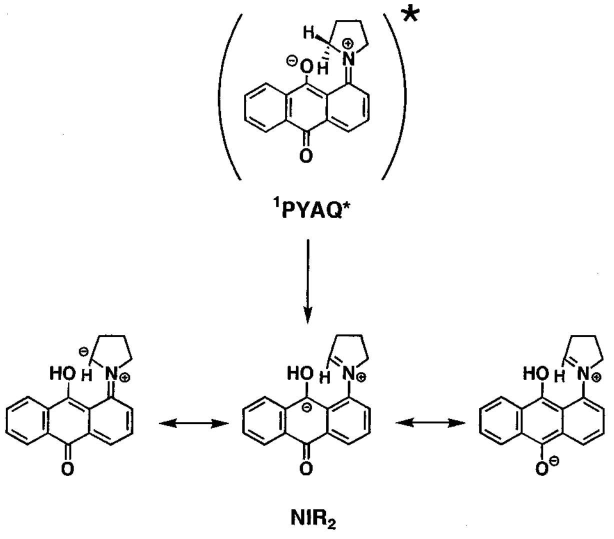


Figure 8. Absorption spectral changes (—) caused by steady-state photolysis of (a,b) PIAQ and (c) PYAQ in ethanol at room temperature. λ_{ex} are the excitation wavelengths and the dotted spectra are recorded by introducing air after photolysis.

SCHEME 3



by steady-state photolysis of anthraquinone and its haloderivatives at room temperature;[4,7] their lowest excited triplet states abstracted a hydrogen atom from the solvent generating the semiquinone radicals (SQR) and disproportionation of two SQR gave rise to formation of the reduced compounds.[3,4b,32,33] Undoubtedly, the photoproduct formed from PXAQ at room temperature can thus be identified to be 1-piperidino- or 1-pyrrodino-9,10-dihydroxyanthracene.[19] By subpicosecond and nanosecond laser photolysis of PXAQ, however, no absorptions due to the lowest excited triplet state (^{3}PXAQ*) and SQR can be seen. This can be ascribed to the fact that photoreduction of PXAQ shown in Figure 8a or 8c is extremely slow compared with that of anthraquinone ($\phi = 1.0$) or its haloderivatives ($\phi = 1.0-0.003$)[4,7] as well as that of 1-methylanthraquinone ($\phi = 0.009$),[2] were ϕ is the quantum yield of photoreduction obtained in ethanol.

Although the absorption spectrum of PXAQ shown in Figure 1 indicates that 405 or ≥510 nm steady-state photolysis of PXAQ should populate ^{1}PXAQ* initially, the resulting photoreduction of PXAQ in ethanol is found to be negligibly slow compared with that caused by 313 nm steady-state photolysis. In connection with this, Inoue et al.[13] reported that 313 nm steady-state photolysis of PIAQ in alkaline aqueous 2-propanol caused photoreduction but no such a reaction was observed by ≥365 or 420 nm photolysis. As shown in Figure 8b, however, the absorption spectral change caused by 366 nm steady-state photolysis of PIAQ in ethanol populating the second excited singlet state initially (cf., Figure 1a) is comparable with that caused by 313 nm steady-state photolysis (cf., Figure 8a).[34]

If 1-piperidino- or 1-pyrrodino-9,10-dihydroxyanthracene is really formed only from ^{3}PXAQ* of a charge-transfer character, all the results obtained so far indicate that intersystem crossing from a higher excited singlet state to a higher excited triplet state followed by cascade internal conversion is the major process for population of ^{3}PXAQ*, i.e., direct ^{1}PXAQ* → ^{3}PXAQ* intersystem crossing is of minute importance owing to its very slow rate compared with that of ^{1}PIAQ* → TRN or ^{1}PYAQ* → NIR$_2$ intramolecular proton transfer. Probably, the higher excited singlet and triplet states may be the second excited singlet state (^{1}PXAQ**) and the third excited triplet state (^{3}PXAQ***), respectively. This is based on the results obtained by picosecond laser photolysis of anthraquinone and its haloderivatives in a solvent with and/or without triethylamine,[5,7] i.e., their lowest excited triplet states [corresponding to the second excited triplet state (^{3}PXAQ**) of PXAQ] are populated by intersystem crossing from the lowest excited singlet states (corresponding to ^{1}PXAQ**) to the second excited triplet states (corresponding to ^{3}PXAQ***) followed by internal conversion.[35]

As reported previously,[6,7] the lowest excited triplet states of anthraquinone and β-haloanthraquinones are of an nπ* character but those of α-haloanthraquinones are of a mixed nπ*-$\pi\pi$* or $\pi\pi$* character owing to the distortion of the geometrical molecular structure caused by the steric hindrance between the carbonyl group and the halogen atom(s). Despite these facts, all the lowest excited triplet states abstract a hydrogen atom from the solvent.[3,4,7] Since the lowest excited triplet states of sterically strained *tert*-butylanthraquinones (the 1,2,3-tri-*tert*-butyl and 1,2-di-*tert*-butyl-3-trimethylsilyl compounds)[9] are also of a mixed nπ*-$\pi\pi$* or $\pi\pi$* character,[3] PXAQ** may be of a similar character owing to the steric hindrance between the carbonyl and piperidino (or pyrrolidino) groups. Hence, additional photoreduction of PXAQ caused by hydrogen-atom abstraction of ^{3}PXAQ** from the solvent cannot be ruled out.

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References and Notes

(1) Nakayama, T.; Hamana, T.; Miki, S.; Hamanoue, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1473.

(2) Nakayama, T.; Torii, Y.; Nagahara, T.; Miki, S.; Hamanoue, K. *J. Phys. Chem. A* **1999**, *103*, 1696.

(3) Hamanoue, K.; Yokoyama, K.; Kajiwara, Y.; Nakajima, K.; Nakayama, T.; Teranishi, H. *Chem. Phys. Lett.* **1984**, *110*, 25. Hamanoue, K.; Nakayama, T.; Tanaka, A.; Kajiwara, Y.; Teranishi, H. *J. Photochem.* **1986**, *34*, 73.

(4) (a) Hamanoue, K.; Sawada, K.; Yokoyama, K.; Nakayama, T.; Hirase, S.; Teranishi, H. *J. Photochem.* **1986**, *33*, 99. (b) Hamanoue, K.; Nakayama, T.; Sawada, K.; Yamamoto, Y.; Hirase, S.; Teranishi, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2735.

(5) Hamanoue, K.; Nakayama, T.; Shiozaki, M.; Funasaki, Y.; Nakajima, K.; Teranishi, H. *J. Chem. Phys.* **1986**, *85*, 5698. Hamanoue, K.; Nakayama, T.; Ito, M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3487. Hamanoue, K.; Nakayama, T.; Asada, S.; Ibuki, K. *J. Phys. Chem.* **1992**, *96*, 3736. Hamanoue, K.; Nakayama, T.; Sasaki, H.; Ikenaga, K.; Ibuki, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3141.

(6) (a) Hamanoue, K.; Kajiwara, Y.; Miyake, T.; Nakayama, T.; Hirase, S.; Teranishi, H. *Chem. Phys. Lett.* **1983**, *94*, 276. (b) Hamanoue, K.; Nakayama, T.; Kajiwara, Y.; Yamaguchi, T.; Teranishi, H. *J. Chem. Phys.* **1987**, *86*, 6654. (c) Hamanoue, K.; Nakayama, T.; Tsujimoto, I.; Miki, S.; Ushida, K. *J. Phys. Chem.* **1995**, *99*, 5802.

(7) Hamanoue, K.; Nakayama, T. *Res. Chem. Intermed.* **1996**, *22*, 189.

(8) Nakayama, T.; Kuramoto, T.; Hamanoue, K.; Teranishi, H. *J. Phys. Chem.* **1986**, *90*, 5689. Nakayama, T.; Hamanoue, K.; Funasaki, Y.; Teranishi, H. *J. Chem. Phys.* **1987**, *87*, 2677.

(9) Nakayama, T.; Yamaguchi, T.; Ushida, K.; Hamanoue, K.; Miki, S.; Matsuo, K.; Yoshida, Z. *Chem. Phys. Lett.* **1988**, *148*, 259. Nakayama, T.; Amijima, Y.; Ushida, K.; Hamanoue, K. *Chem. Phys. Lett.* **1996**, *258*, 663.

(10) Nakayama, T.; Shimizu, T.; Torii, Y.; Miki, S.; Hamanoue, K. *J. Photochem. Photobiol. A: Chem.* **1997**, *111*, 35. Nakayama, T.; Torii, Y.; Shimizu, T.; Miki, S.; Hamanoue, K. *Chem. Lett.* **1998**, 145.

(11) Nakayama, T.; Nagahara, T.; Miki, S.; Hamanoue, K. *Chem. Phys. Lett.* **1997**, *266*, 601. Nagahara, T.; Nakayama, T.; Miki, S.; Hamanoue, K. *J. Photochem. Photobiol. A: Chem.* **1999**, *124*, 47.

(12) Nakayama, T.; Torii, Y.; Nagahara, T.; Hamanoue, K. *J. Photochem. Photobiol. A: Chem.* **1998**, *119*, 1.

(13) Inoue, H.; Kawabe, K.; Kitamura, N.; Hida, M. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1874.

(14) Nakayama, T.; Amijima, Y.; Ibuki, K.; Hamanoue, K. *Rev. Sci. Instrum.* **1997**, *68*, 4364.

(15) Ushida, K.; Nakayama, T.; Nakazawa, T.; Hamanoue, K.; Nagamura, T.; Mugishima, A.; Sakimukai, S. *Rev. Sci. Instrum.* **1989**, *60*, 617.

(16) Inoue, H.; Hida, M.; Nakashima, N.; Yoshihara, K. *J. Phys. Chem.* **1982**, *86*, 3184.

(17) Riddick, J. A.; Bunger, W. B. *Technique of Chemistry, Vol., Organic Solvents,* 3rd ed.; Wiley-Interscience: New York, 1970.

(18) Yoshida, Z.; Takabayashi, F. *Tetrahedron* **1968**, *24*, 933.

(19) Davies, A. K.; McKellar, J. F.; Phillips, G. O. *Proc. R. Soc. London* **1971**, *A323*, 69.

(20) Hulme, B. E.; Land, E. J.; Phillips, G. O. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1992, 2003.

(21) Yamauchi, R.; Nakayama, T.; Hamanoue, K. *Abstracts of Symposium on Photochemistry* 1999, p 93, Okayama, Japan.

(22) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.

(23) Ooshika, Y. *J. Phys. Soc. Jpn.* **1954**, *9*, 594.

(24) Lippert, E. Z. *Naturforsch.* **1955**, *A10*, 541.

(25) McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562.

(26) Mataga, N.; Kubota, T. *Molecular Interaction & Electronic Spectra*; Mercel Dekker: New York, 1970; p 371.

(27) According to Horng et al.,[22] however, the aromatic solvents offer a solvation mechanism different from that of the other solvents.

(28) Gritsan, N. P.; Shvartsberg, E. M.; Russkikh, V. V.; Khmelinski, I. V. *Russ. J. Phys. Chem.* **1990**, *64*, 1660 (translated from *Zh. Fiz. Khim.* **1990**, *64*, 3081). Gritsan, N. P.; Khmelinski, I. V.; Usov, O. M. *J. Am. Chem. Soc.* **1991**, *113*, 9615.

(29) Johnson, A. W. Ylid Chemistry. In *Organic Chemistry*; Blomquist, A. T., Ed.; Academic Press: New York, 1966; Vol. 7, Part 2, Chapter 7.

(30) On the basis of the present study, the tentative assignment of band A to the absorption due to the lowest excited singlet state of NIR$_1$ as well as estimation of the shift time (∼10 ns) of band A reported in the previous Letter[31] are incorrect.

(31) Nakayama, T.; Nagai, N.; Torii, Y.; Hamanoue, K. *Chem. Lett.* **1999**, 33.

(32) Wilkinson, F. *J. Phys. Chem.* **1962**, *66*, 2569. Tickle, K.; Wilkinson, F. *Trans. Faraday Soc.* **1965**, *61*, 1981.

(33) Carlson, S. A.; Hercules, D. M. *Photochem. Photobiol.* **1973**, *17*, 123.

(34) For PYAQ in ethanol at room temperature, however, 366 nm steady-state photolysis causes extremely slow photoreduction compared with that caused by 313 nm steady-state photolysis.

(35) Inoue et al.[13] proposed that ^{3}PIAQ** was populated via intersystem crossing from a higher excited singlet state to a higher excited triplet state followed by internal conversion in the triplet manifold(s). This can be ruled out on the basis of the present result obtained by 366 nm steady-state photolysis.