

Mechanism for Photocleavage of *N*-(Anthroyloxy)-9-fluorenylideneamines and Dynamic Behavior of Anthroyloxy Radicals

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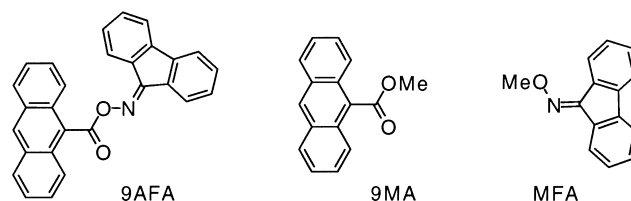
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Photocleavage of the N–O bond of *N*-(9-anthroyloxy)-9-fluorenylideneamine and its 1- and 2-anthroyloxy derivatives takes place efficiently in acetonitrile in the excited singlet state attributed to the fluorenylidene moiety. This made it possible for the first time to directly observe anthroyloxy radicals by the transient absorption method. The quantum efficiency for photocleavage decreases remarkably in benzene, in which the lowest excited singlet state is attributed to the anthroate moiety. All the three kinds of anthroyloxy radicals are much less reactive in decarboxylation, addition to olefins, and hydrogen-atom abstraction than benzoyloxy and 1- and 2-naphthoyloxy radicals; 9-anthroyloxy radicals supposedly undergo intramolecular addition–elimination in the ipso-position in equilibrium with α -lactonic spirodihydroanthryl radicals, as indicated by one-color and two-color laser photolyses.

Diaroyl peroxides are useful precursors of aroyloxy radicals and have been used for studies on various kinds of benzoyloxy and naphthoyloxy radicals.^{1–10} As previously studied in photolyses of the peroxides, the decarboxylation of benzoyloxy radicals is accelerated by introduction of methyl groups or chlorine atoms in the two ortho-positions resulting in twisting of the carbonyloxy group from the molecular plane on account of steric hindrance.^{3,4} On the contrary, the decarboxylation rate of 1-naphthoyloxy radicals is reduced by their conjugate ring system, which is wider than in the case of benzoyloxy radicals.⁵

Anthroyloxy (anthracenecarbonyloxy) radicals are attractive species to study, since they have a more expanded conjugate ring system and the carbonyloxy moiety suffers varying extents of steric hindrance to become more or less twisted from the molecular plane depending on its attached ring position. Among some anthroate (anthracenecarboxylate) esters of aromatic and aliphatic ketoximes employed as precursors instead of intractable peroxides, only fluorenone oxime esters have been found to produce the anthroyloxy radicals efficiently in polar solvents. According to the previously proposed triplet mechanism,^{11–13} the fluorenone oxime esters should be less reactive than acetophenone and benzophenone oxime esters.

In order to get further insight into the electronic and steric effects on the reactivity of aroyloxy radicals, we have firstly clarified the mechanism of photocleavage of the radical precursors, *N*-(anthroyloxy)-9-fluorenylideneamines, from the viewpoints of solvent and excitation wavelength effects.¹⁴ Then we studied the behavior of the anthroyloxy radicals in solution by means of transient absorption spectroscopy.¹⁵ In this paper we discuss the photocleavage mechanism of the oxime esters and the structure-reactivity relationships of 1-, 2-, and 9-anthroyloxy radicals.



Scheme 1.

Results and Discussion

1. Photocleavage of the Oxime Esters. *N*-(9-Anthroyloxy)-9-fluorenylideneamine (9AFA, Scheme 1) exhibits absorption bands around 300 and 365 nm in acetonitrile and benzene. In comparison with the spectra of *N*-methoxy-9-fluorenylideneamine (MFA) and 9-methoxycarbonylanthracene (9MA), these bands are attributed to π – π^* transitions of the fluorenylidene and anthroate moieties, respectively, though the 300-nm band is slightly blue-shifted from MFA's band, and the 365-nm band slightly red-shifted from 9MA's and overlapped with a weak n – π^* band of the fluorenylidene moiety (Fig. 1). Similar features of the absorption spectra were observed for *N*-(1-anthroyloxy)- (1AFA) and *N*-(2-anthroyloxy)-9-fluorenylideneamines (2AFA, Scheme 2). However, spectral profiles of the longer wavelength bands depend on the structure of AFAs: structured for 2AFA and 9AFA, but structureless for 1AFA. These features are common to 1-methoxycarbonyl- (1MA), 2-methoxycarbonylanthracenes (2MA), and 9MA.

9AFA was photolyzed with 365-nm stationary light in a low concentration (1×10^{-3} mol dm^{–3}) in acetonitrile under argon at ambient temperature to give 9-anthraic (9-anthracenecarboxylic) acid (9AA; 0.92 mol/mol 9AFA) and 9-fluorenone azine (FAz; 0.42) as products (Scheme 3). Similar irradiation of 9AFA at 300 nm gave almost the same results, as shown in

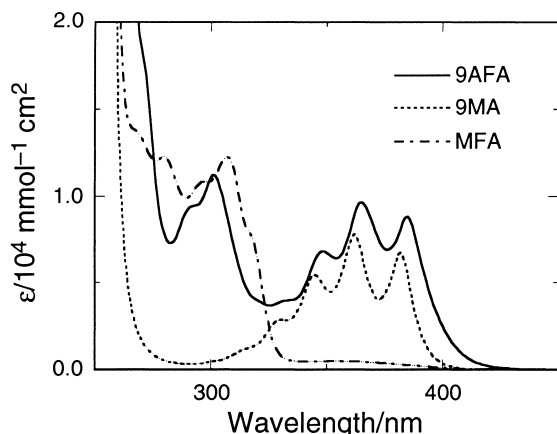
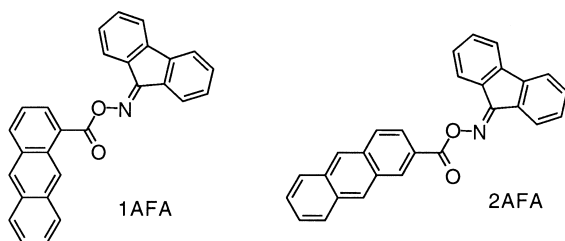


Fig. 1. Absorption spectra of 9AFA, 9MA, and MFA in acetonitrile.



Scheme 2.

Table 1. Product Yields (mol/mol AFA) in Photolysis of AFAs in Acetonitrile and Benzene

AFA	Light/nm	AA	FAz
In acetonitrile			
1AFA	300	0.93	0.44
	366	0.90	0.41
2AFA	300	0.92	0.45
	366	0.93	0.45
9AFA	300	0.83	0.41
	366	0.92	0.42
In benzene			
1AFA	300	0.14	0.22
2AFA	300	0.14	0.18
9AFA	300	0.26	0.35

Table 1. The formation of FAz indicates intermediacy of 9-fluorenylideneaminyl radicals,¹¹ which must be generated together with 9-anthroyloxyl radicals (9-AnCO₂•) via homolysis of the N-O bond of 9AFA (Scheme 4). Since anthracene was not

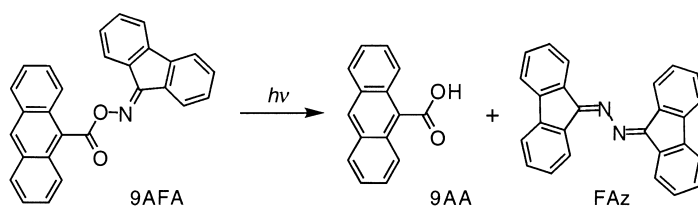
detected in the products at all with either 300- or 365-nm light, 9-AnCO₂• seems not to undergo decarboxylation at ambient temperature.

1AFA and 2AFA were also photolyzed under similar conditions to give the corresponding acids (1AA and 2AA, respectively) and FAz in good yields, as shown in Table 1. These results suggest that the excitation of AFAs in either chromophore results in the N-O bond cleavage to give the iminyl and the corresponding anthroyloxyl radicals, and that the former dimerize to give FAz and the latter undergo hydrogen-atom abstraction from the solvent to give the acids.

Stationary photolyses of AFAs were also performed in benzene. AAs and FAz were found to be the major products, but their yields were much lower than those in acetonitrile (Table 1). Several minor products were detected by HPLC, but their structures have not been determined.

2. Direct Observation of the Radical Species. Pulsed laser photolysis of 9AFA (5×10^{-4} mol dm⁻³) at 308 nm under argon in acetonitrile at ambient temperature exhibited transient absorption bands at 400–500 and 500–800 nm, as shown in Fig. 2. Similar laser photolysis of 9AFA at 360 nm gave almost the same spectrum.¹⁴ The longer-wavelength band displayed essentially identical decay time constants of 8–10 μs at 580, 630, 680, and 720 nm, and can be reasonably assigned to 9-AnCO₂• by comparison with the spectra of 2,6-dimethylbenzoyloxyl and other aryloxyl radicals.^{2–8} For this band, molecular oxygen neither reduced spectral intensity nor affected spectral and decay profiles. These facts not only support the above assignment of the oxygen-centered radicals but also indicate that excited triplet states are not involved in the radical formation, i.e., N-O bond cleavage. The spectral assignment was also supported by two-color laser photolysis of 9AFA. Upon 308 plus 580 nm laser photolysis, the latter pulse induced a rapid decrease in intensity of the initially rising band, as monitored at 570, 630, 680, and 720 nm. This phenomenon can be ascribed to photoinduced decarboxylation of 9-AnCO₂•, as described in Subsection 4. Thus, the whole longer wavelength band is assigned to a single species, 9-AnCO₂•.

An identical transient absorption band was also observed in the 500–800 nm region on laser photolysis of 1-(9-anthroyloxy)-2-pyridone (9APy; 3.0×10^{-4} mol dm⁻³) at 308 nm in acetonitrile (Scheme 5, Fig. 3). In Fig. 3 an absorption band due to 2-pyridyloxyl radicals is overlapped around 390 nm.^{16,17} This spectral identity confirms the above assignment, since a series of 1-benzoyloxy- and 1-(naphthoyloxy)-2-pyridones have been shown to be photochemically dissociated into benzoyloxyl¹⁷ and naphthoyloxyl radicals¹⁸ and 2-pyridyloxyl radicals. Actually, in the case of 9APy with 300-nm light, the formation of 9AA (0.51 mol/mol 9APy) and 2-pyridone (0.61)



Scheme 3.

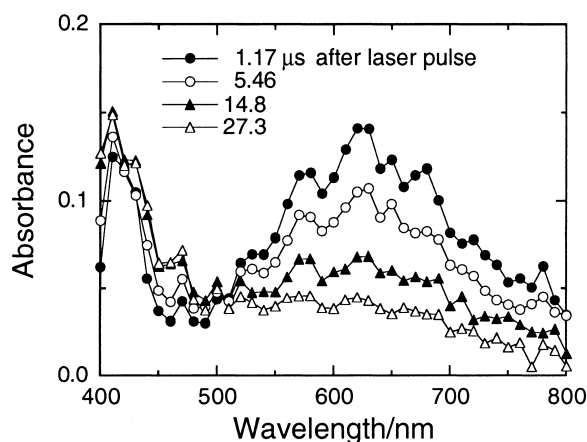
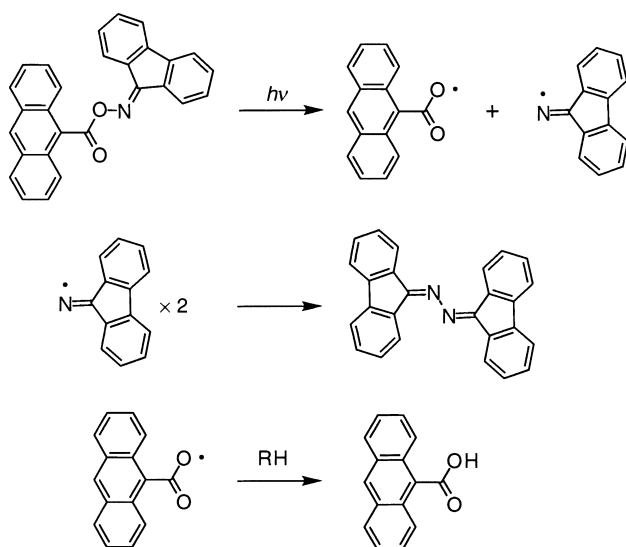
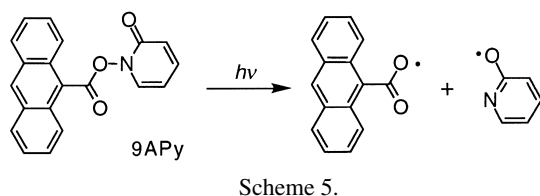


Fig. 2. Transient absorption spectra observed on 308-nm pulsed laser excitation of 9AFA in acetonitrile under argon.



was confirmed in the product analysis with HPLC.

Pulsed laser photolysis of 1AFA and 2AFA (5×10^{-4} mol dm^{-3}) at 308 and 360 nm under similar conditions exhibited characteristic transient absorption bands, as shown in Figs. 4 and 5, respectively. These bands can be assigned to 1- and 2-anthroyloxy radicals, respectively, since their spectra and time profiles were not affected by oxygen at all, and essentially identical bands were observed on laser photolysis of 1-(1-anthroyloxy)- (1APy) and 1-(2-anthroyloxy)-2-pyridones (2APy), respectively, at 308 nm under similar conditions. The

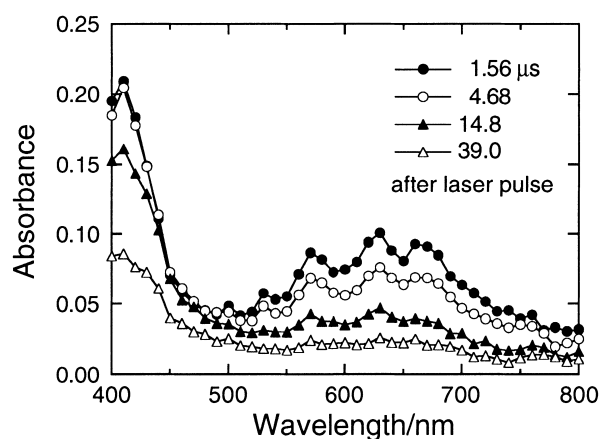


Fig. 3. Transient absorption spectra observed on 308-nm pulsed laser excitation of 9APy in acetonitrile under argon.

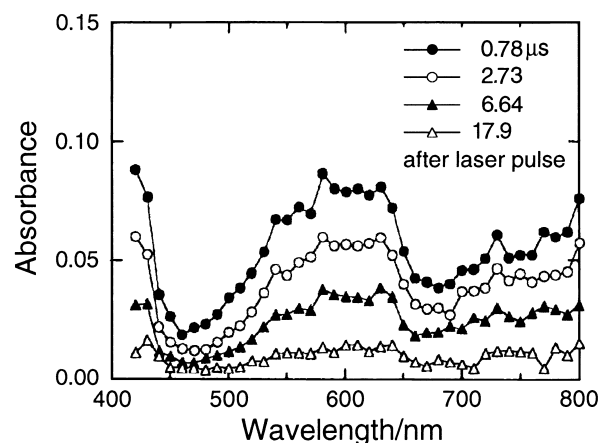


Fig. 4. Transient absorption spectra observed on 308-nm pulsed laser excitation of 1AFA in acetonitrile under argon.

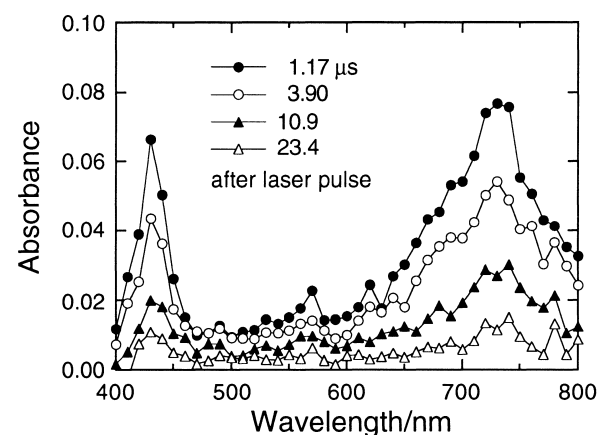
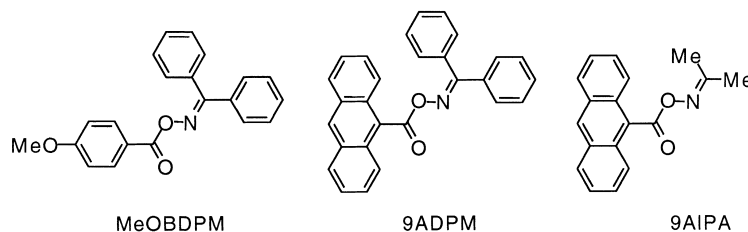


Fig. 5. Transient absorption spectra observed on 308-nm pulsed laser excitation of 2AFA in acetonitrile under argon.

lifetimes of the observed radicals are summarized in Table 2.

3. Mechanism for Photocleavage of the Oxime Esters. The quantum yields for photocleavage of 9AFA ($1-3 \times 10^{-4}$



Scheme 6.

Table 2. Lifetimes of Anthroyloxy Radicals Generated from 360-nm Laser Photolysis of AFAs and 308-nm Laser Photolysis of APys in Acetonitrile at Ambient Temperature

Radical	Precursor	Lifetime/ μs^{a}
1-AnCO ₂ [•]	1AFA	9.9
	1APy	10
2-AnCO ₂ [•]	2AFA	14
	2APy	14
9-AnCO ₂ [•]	9AFA	6.5
	9APy	6.3

a) Monitored at 580 and 720 nm for 1-AnCO₂[•], 720 nm for 2-AnCO₂[•], and 580 and 630 nm for 9-AnCO₂[•].

Table 3. Quantum Yields for Photocleavage of AFAs in Acetonitrile and Benzene

AFA	Light/nm	Solvent	
		MeCN	PhH
1AFA	302	0.09	0.004
	365	0.10	0.003
2AFA	302	0.12	0.003
	365	0.11	0.002
9AFA	302	0.10	0.035
	365	0.09	0.014

mol dm⁻³) were determined from consumption of the starting material with 302- and 365-nm light in acetonitrile and benzene. The results are summarized in Table 3 together with those for 1AFA and 2AFA. In the above concentration range, the quantum yields were not affected. In acetonitrile the quantum yields are around 0.1 for all the three AFAs and are independent of the irradiation wavelengths. In benzene, however, the quantum yields are lower, particularly for 1AFA and 2AFA, and for 9AFA the quantum yield depends on the irradiation wavelength; it is higher at 302 nm than at 365 nm. It is noticeable that the quantum yield is dependent on the solvents and the excitation wavelengths, suggesting that the energy levels of the two chromophores change between the polar and nonpolar solvents.

Pulsed laser photolysis of 9AFA (5×10^{-4} mol dm⁻³) at 444 nm in acetonitrile in the presence of biacetyl (1×10^{-2} mol dm⁻³) as a triplet sensitizer exhibited an absorption band around 430 nm with a lifetime of 7.8 μs , but none of the absorption bands assignable to 9-anthroyloxy radicals was detected. The observed band is very similar to the T-T absorption of 9MA (lifetime 8.5 μs), and can be assigned to the triplet state of the anthroate moiety. Since the triplet excitation ener-

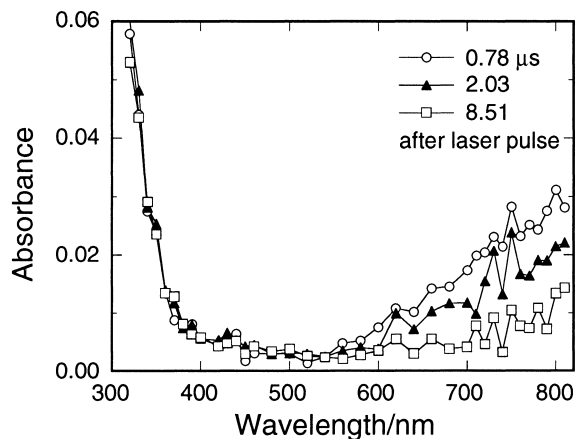


Fig. 6. Transient absorption spectra observed on 308-nm pulsed laser excitation of MeOBDPM in acetonitrile under argon.

gy of biacetyl (236 kJ mol^{-1})¹⁹ is higher than those of anthroic acid (177)¹⁹ and 9-fluorenone (211),¹⁹ this observation suggests that the photocleavage of 9AFA takes place from the excited singlet state but not from the excited triplet state. This is consistent with the fact that the spectral intensity of 9-anthroyloxy radicals was not affected by molecular oxygen.

The involvement of the excited singlet state in the photocleavage of the present oxime esters is in contrast to the triplet mechanism, which was previously proposed for photocleavage of a series of oxime esters such as *N*-(*p*-methylbenzoyloxy)diphenylmethanimine.^{11–13} In this study we have carried out pulsed laser photolysis of *N*-(*p*-methoxybenzoyloxy)-(MeOBDPM), *N*-(9-anthroyloxy)diphenylmethanimines (9ADPM), and *N*-(9-anthroyloxy)isopropylideneamine (9AIPA) (Scheme 6). Upon laser photolysis at 308 nm, MeOBDPM showed absorption bands in the wavelength regions of 300–400 and 600–800 nm (Fig. 6). In Fig. 6, the shorter and longer wavelength bands are long- (lifetime >300 μs) and short-lived (5.5 μs), respectively, and the latter is ascribed to *p*-methoxybenzoyloxy radicals after comparison with the spectrum from bis(*p*-methoxybenzoyl) peroxide.²⁶ The former can be, therefore, ascribed to the pair radicals, diphenylmethaniminyls. For 9ADPM and 9AIPA, a strong band due to the anthroate triplets was observed at <450 nm; however, the intensities were not enough in the 500–800 nm region to identify the spectrum. The structure dependence of the photocleavage efficiency can be interpreted in terms of the triplet energies of the imines;¹³ in the methoxybenzoyloxy derivative the lowest triplet is located in the diphenylmethanimino moiety, but in the anthroyloxy derivatives it is in the anthroate moiety. The triplet energy of the

Table 4. Features of Fluorescence Spectra of AFAs and MAs in Acetonitrile and Benzene; Fluorescence Maxima ($\lambda_{\text{max}}^{\text{e}}$ /nm), Singlet Excitation Energies (E_{S} /kJ mol⁻¹), Quantum Yields (ϕ_{f}), and Lifetimes (τ_{f} /ns)

AFA	Solvent	$\lambda_{\text{e,max}}$		E_{S}		ϕ_{f}	τ_{f}
1AFA	MeCN	457	464 ^{a)}	284 ^{b)}	286	0.02	0.46
	PhH	463	462 ^{a)}	282 ^{b)}	282	0.23	8.0
2AFA	MeCN	438	465 ^{a)}	289 ^{b)}	291	0.02	0.86
	PhH	463	462 ^{a)}	285 ^{b)}	285	0.04	7.5
9AFA	MeCN	463	485 ^{a)}	291 ^{b)}	296	0.01	1.1
	PhH	465	471 ^{a)}	290 ^{b)}	291	0.05	7.8
1MA	MeCN	453		291		0.64	15.5
	PhH	446		291		0.54	8.8
2MA	MeCN	435		297		0.97	22.7
	PhH	432		297		0.90	16.6
9MA	MeCN	459		301		0.31	8.2
	PhH	455		299		0.69	12.4
MFA	MeCN	466		291 ^{b)}	293	0.001	3.4
	PhH	461		293		0.001	4.1

a) Excitation wavelength: 300 nm. b) From fluorescence spectra observed on 300 nm excitation.

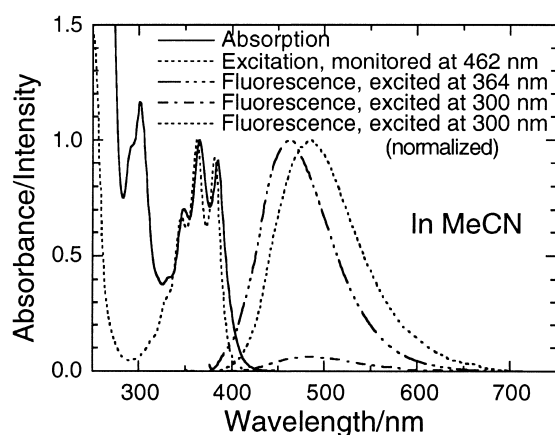


Fig. 7. Absorption, fluorescence, and fluorescence excitation spectra of 9AFA in acetonitrile. The spectra were normalized at a band maximum except for the fluorescence spectrum measured on 300-nm excitation; this spectrum was depicted relative to the fluorescence spectrum measured on 364-nm excitation.

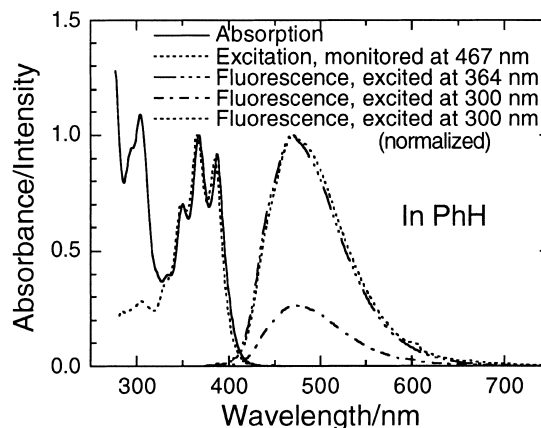


Fig. 8. Absorption, fluorescence, and fluorescence excitation spectra of 9AFA in benzene. The spectra were normalized at a band maximum except for the fluorescence spectrum measured on 300-nm excitation; this spectrum was depicted relative to the fluorescence spectrum measured on 364-nm excitation.

photoreactive MeOBDPM is assumed to be larger than the dissociation energy of the N-O bond, but those of 9ADPM and 9AIPA are assumed to be smaller.¹³

The fluorescence spectra of 9AFA (1×10^{-4} mol dm⁻³) are structureless and very similar to those of 9MA (1×10^{-4} mol dm⁻³) in acetonitrile (Fig. 7) and benzene (Fig. 8), respectively, on excitation at 364 nm. The fluorescence quantum yield (ϕ_{f}) and lifetime (τ_{f}) of 9AFA were, however, much lower and shorter, respectively, than those of 9MA in acetonitrile and benzene, as shown in Table 4. The results were not affected up to a substrate concentration of 1×10^{-4} mol dm⁻³. These results suggest that the anthroate singlet is efficiently quenched by the fluorenylidene moiety. 1AFA and 2AFA showed almost the same fluorescence quantum yields in acetonitrile as did 9AFA. The features of the fluorescence spectra are summarized in Table 4.

The strong interaction between the two chromophores in the

excited singlet state was confirmed by quenching of the 9MA fluorescence by MFA; linear Stern-Volmer plots of the fluorescence lifetimes gave quenching rate constants (k_{q}) of 2.4×10^{10} and 1.5×10^{10} mol⁻¹ dm³ s⁻¹ in acetonitrile and benzene, respectively. These diffusion-controlled rate constants are quite reasonable if one takes into account the fact that the singlet energy of 9MA is larger than that of MFA (vide infra) and that one finds a very small spectral overlap of the 9MA fluorescence and MFA absorption.

The singlet excitation energies (E_{S}) of 9AFA, 9MA, and MFA were estimated from the absorption and fluorescence spectra, as listed in Table 4. As mentioned above, 9AFA and 9MA exhibit similar fluorescence spectra. Their E_{S} values are estimated to be 296 and 301 kJ mol⁻¹, respectively, from their absorption and fluorescence spectra, which were measured by exciting at 364 nm in acetonitrile. These values can be ascribed to the anthroate moiety. Upon 300-nm excitation,

9AFA exhibited a weak fluorescence spectrum more than 20 nm red-shifted from that observed on 364-nm excitation (Fig. 7), and this spectrum gives a slightly lower E_s value of 291 kJ mol⁻¹. This value is identical with that for MFA, and can be ascribed to the fluorenylidene moiety.

The fluorescence excitation spectrum of 9AFA monitored at the emission peak of 462 nm in acetonitrile shows a 365-nm band profile almost identical with the absorption band but slightly shifted to the shorter wavelengths, as shown in Fig. 7. However, no clear peak appeared around 300 nm, though the absorption spectrum exhibits a band due to the fluorenylidene moiety in this region. These observations indicate that the 300-nm excitation results in the excited singlet state located in the fluorenylidene moiety through internal conversion from a higher excited singlet state, and that the 364-nm excitation leads to the initial formation of the excited singlet state of the anthroate moiety, followed by energy transfer to the fluorenylidene moiety, to result in the fluorenylidene excited singlet; the initially formed anthroate singlet is responsible for the fluorescence emission. Thus, the lowest (S_1) and the second excited singlet state (S_2) of 9AFA are assigned to the fluorenylidene and anthroate moieties, respectively.

In benzene, the absorption spectrum of 9AFA is slightly red-shifted compared with that in acetonitrile, and the fluorescence spectrum is not affected by the excitation wavelengths of 300 and 364 nm. These facts suggest a significantly lower E_s value (290 kJ mol⁻¹) for the anthroate moiety compared with the above E_s in acetonitrile. The excitation spectrum of 9AFA exhibited a weak but clear band around 300 nm (Fig. 8), indicating that the initial excitation of the fluorenylidene moiety results in a partial population of the excited singlet in the anthroate moiety. Thus the lowest excited singlet state is attributed to the anthroate moiety. Since the excited singlet level of MFA is estimated to be about 293 kJ mol⁻¹, the S_2 state of 9AFA is assigned to the fluorenylidene moiety, but the energy difference between S_1 and S_2 may be quite small. The reversion of the two singlet energy levels due to the anthroate and fluorenylidene moieties in acetonitrile and benzene is consistent with the observed solvent dependence of the quantum yields for photocleavage of 9AFA, lower in benzene and higher in acetonitrile (Table 3). Inspection of absorption and fluorescence spectra of 9MA and MFA indicates that the difference in the singlet energy between 9MA and MFA is larger in acetonitrile than in benzene, though the singlet level of 9MA is higher than that of MFA in both solvents.

Schematic energy diagrams are depicted in Fig. 9. In benzene the lowest excited singlet states of the fluorenylidene ($S_2(F)$) and the anthroate ($S_1(A)$) moieties are similar in energy. However, in acetonitrile the lowest excited singlet state of the fluorenylidene moiety ($S_1(F)$) is clearly lower than that of the anthroate moiety ($S_2(A)$) and may be responsible for the N–O cleavage. Thus, the irradiation of 9AFA at 300 nm (ca. 400 kJ mol⁻¹) in acetonitrile results in the formation of a higher excited singlet state of the fluorenylidene moiety (probably $S_3(F)$; Fig. 9) followed by its internal conversion to the lowest excited singlet state, $S_1(F)$ (E_s ca. 290 kJ mol⁻¹), which undergoes N–O bond cleavage to give the radicals. The weak fluorescence results predominantly from $S_1(F)$. On the contrary, the irradiation at 365 nm produces the $S_2(A)$ state (ca. 300 kJ

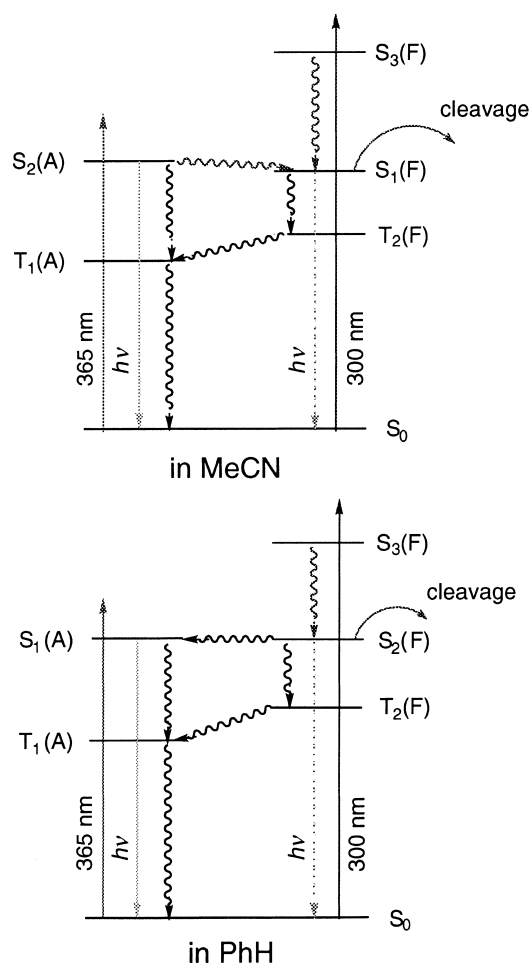


Fig. 9. Schematic energy diagrams of 9AFA in the polar and the nonpolar solvent.

mol⁻¹), which undergoes fluorescence emission or energy transfer to the fluorenylidene moiety to give $S_1(F)$, leading to the N–O bond cleavage. In benzene, the $S_2(F)$ state produced by 300-nm irradiation followed by internal conversion undergoes predominantly energy transfer to the anthroate moiety to produce $S_1(A)$, which undergoes fluorescence emission or intersystem crossing to give eventually the $T_1(A)$ state; thus the N–O cleavage is less efficient.

1AFA and 2AFA were also photocleaved more efficiently in acetonitrile than in benzene (Table 3). The E_s values of 9MA, 2MA, and 1MA decrease in this order (301 → 297 → 291 kJ mol⁻¹ in acetonitrile), as shown in Table 4. The E_s values for the anthroate moieties in 9AFA, 2AFA, and 1AFA are lower than those of MAs, respectively, and also decrease in this order (296 → 291 → 286 kJ mol⁻¹). For 1AFA and 2AFA as well as 9AFA, the E_s values ascribable to the fluorenylidene moiety are slightly lower (291, 289, and 284 kJ mol⁻¹ for 9AFA, 2AFA, and 1AFA, respectively) than E_s 's due to the anthroate moiety, as estimated from the absorption spectra and the fluorescence spectra measured with 300-nm excitation light. Thus, the features of the energy levels of $S_2(A)$ and $S_1(F)$ in 1AFA and 2AFA are similar to those of 9AFA. In benzene, 1AFA and 2AFA exhibited almost identical fluorescence spectra independently of the excitation wavelengths at 300 and 364 nm

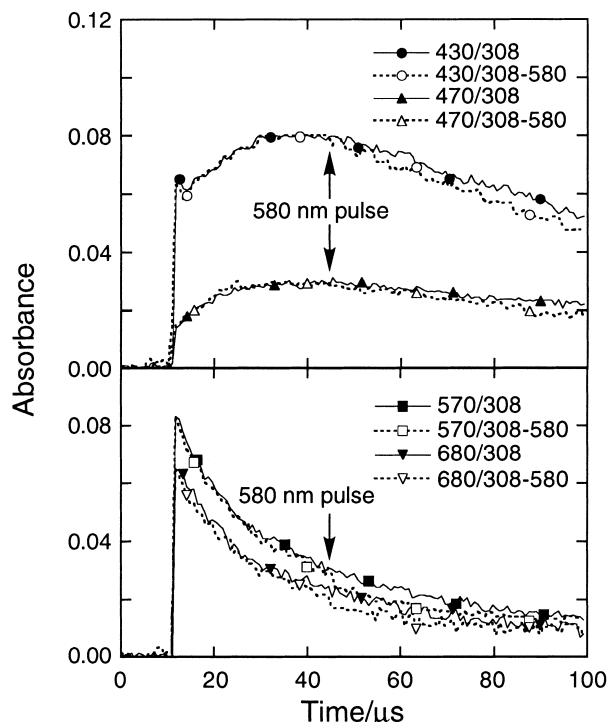
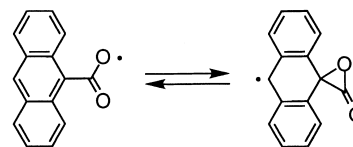


Fig. 10. Time profiles of the transient absorption spectra monitored at different wavelengths on one-color and two-color laser photolysis of 9AFA at 308 (+580) nm in acetonitrile under argon.

and at 300 and 358 nm, respectively; the spectra are due to the anthroate moiety. The E_S values of the S_1 states are estimated to be 282 and 285 kJ mol⁻¹ for 1AFA and 2AFA, respectively. The E_S values of the S_2 states for the fluorenylidene moiety are assumed to be nearly 291 kJ mol⁻¹ or slightly lower. Thus, the energy difference between S_2 and S_1 may be larger in 1AFA and 2AFA than in 9AFA. These observations are consistent with the aforementioned solvent dependence of the quantum yields, and similar reaction mechanisms may be operative in the three isomers.

4. Dynamic Behavior of 9-Anthroyloxyl Radicals. In Fig. 2, the shorter wavelength band observed in the laser photolysis of 9AFA may be ascribed to a plural species, such as 9AFA triplets, 9-fluorenylideneaminyll radicals, and an intermediate derived from 9-AnCO₂[•]. Inspection of the time profiles of the spectrum at 430 and 470 nm (Fig. 10; 308-nm photolysis) indicates that there are at least two rise components, a fast one (within the instrumental detection limit) and a slow one. The fast component can be assigned to 9AFA triplets on the basis of the results that the fast rise was almost completely quenched under oxygen and that the triplet sensitization with biacetyl exerted only a T-T absorption due to the anthroate moiety at 430 nm. The slow component grows with a time constant of ca. 10 μs with a concomitant decay of the longer wavelength band with an isosbestic point around 500 nm (Fig. 2), and then decays with a time constant of ca. 100 μs. The decay of the longer wavelength band is composed of two components with time constants of 8–10 and 90–100 μs. In the presence of cyclohexene, which accelerated the decay of the longer



Scheme 7.

wavelength band, the increment of the slow component decreased with increasing the olefin concentration (cf. Subsection 6). This fact can be interpreted in terms of the reaction of 9-AnCO₂[•] with cyclohexene to reduce the intermediate formation.

As for the structure of the intermediate, 9,10-dihydro-9-anthryl radicals derived from 9,10-dihydroanthracene have an absorption band around 350 nm,²⁰ and the present intermediate may exhibit a band maximum at the wavelengths shorter than 400 nm. Thus, we tentatively assign this intermediate to an α -lactonic oxiran-2-one-3-spiro-9'-(9',10'-dihydroanthracen)-10'-yl radical, which is produced through an intramolecular addition of the oxygen-centered radical to the ipso-position (Scheme 7). As will be described below, a twisted geometry of 9-AnCO₂[•] may promote this process. Intermediacy of similar α -lactonic radicals was previously proposed in the thermolysis of di(1-naphthoyl) peroxide.²¹

Analysis of the time profiles of the transient absorptions suggests that the α -lactonic radicals are in addition-elimination equilibrium with the original 9-AnCO₂[•] radicals, which eventually abstract a hydrogen atom to give the anthroic acid. This is an intramolecular case of the reversible addition of aroyloxyl radicals to aromatic substrates.²² As mentioned above, the diphenylmethaniminyl radicals are assumed to have an absorption band in the 300–400 nm region. For 9AFA and other AFAs, however, no absorption bands assignable to 9-fluorenylideneaminyll radicals were detected in the wavelengths longer than 400 nm.²³

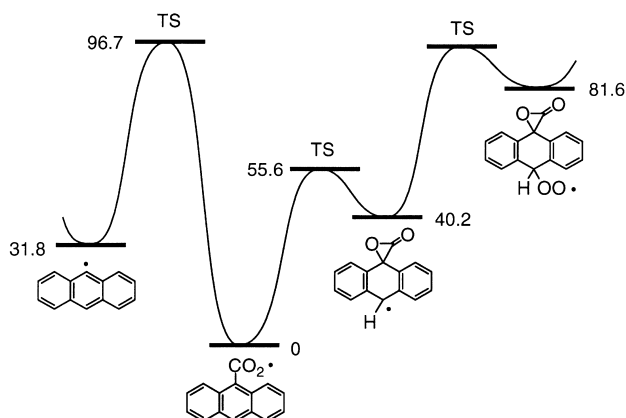
The addition-elimination equilibration of 9-AnCO₂[•] was examined by means of the two-color laser photolysis. This is based on the fact that the decarboxylation of 9-AnCO₂[•] is induced by light irradiation. Actually, on laser excitation of 9AFA with 308 nm pulses in acetonitrile, the yield of anthracene as a decarboxylation product increased and that of anthroic acid decreased with increasing the laser power, as shown in Table 5. The two-color photolysis of 9AFA with 308 plus 580-nm laser pulses also produced anthracene at the expense of anthroic acid (Table 5).

Pulsed laser excitation of 9-AnCO₂[•] in the two-color photolysis of 9AFA with a 308-nm laser pulse followed by a 580-nm laser pulse with a 35-μs delay caused a rapid loss in absorbance, for example, at 570 and 680 nm and a gradual loss at 430 and 470 nm, as shown in Fig. 10. The rapid loss in absorbance in the longer wavelengths corresponds to the decrease of 9-AnCO₂[•] concentration by photoinduced decarboxylation, and the concomitant gradual loss in the shorter wavelengths is rationalized by a shift of the equilibrium to the 9-AnCO₂[•] side caused by the decrease of 9-AnCO₂[•] concentration.

The time profile of the slow rise component in the shorter wavelengths was not affected much under oxygen atmosphere. This observation means that the α -lactonic radical is almost

Table 5. Yields of Anthracene (AH) and Anthroic Acids (AA) in 308 nm One-Color and 308 + 580 nm Two-Color Laser Photolyses of AFAs in Acetonitrile

Precursor	Laser/nm	Power/mJ pulse ⁻¹	Yield/%	
			AH	AA
9AFA	308	40	38	52
		13	25	68
		4	10	73
		4	9	67
	308 + 580	4 + 7	16	62
9APy	308	13	26	70
1AFA	308	40	4	84
2AFA	308	40	11	77

Fig. 11. Calculated energy surfaces for 9-AnCO₂•. The figures refer to energies in kJ mol⁻¹ relative to that of 9-AnCO₂•.

unreactive towards oxygen. This apparent loss of reactivity with oxygen might be due to its equilibration with the anthroyloxyl radical, which has no reactivity with oxygen (cf. Subsection 5). Recently, some diaryl- and triarylmethyl radicals were reported to be unreactive towards molecular oxygen.²⁴

5. Theoretical Approach to the Behavior of 9-Anthroyloxyl Radicals. Geometries of the anthroyloxyl radicals were optimized by use of UHF/PM3 and UB3LYP/6-31G* calculations. For 9-AnCO₂• and 2-AnCO₂• a geometry perpendicularly twisted at the C_{ipso}-C_α bond and a planar geometry were optimized, respectively, by both methods. For 1-AnCO₂• a nearly 60° twisted geometry was optimized by the UHF/PM3 method; however, the DFT method predicted that the energy minima were located at a twisted and a planar geometry but the former was slightly higher in energy than the latter. The DFT-optimized geometry of 9-AnCO₂• has a C_{ipso}-C_α bond significantly longer (151.2 pm) than those for 1- and 2-AnCO₂• (147.3 and 146.9 pm, respectively). As for the relative energy, the planar 1- and the twisted 9-AnCO₂• are 7.5 and 7.1 kJ mol⁻¹ higher than the planar 2-AnCO₂•, respectively.

The energy surfaces for the reactions of 9-AnCO₂• and the α-lactonic radical were estimated as shown in Fig. 11. The UHF/PM3 calculations predict that the energies (heats of formation) of the α-lactonic radical and the anthryl radical (plus a CO₂ molecule) are 40.2 and 31.8 kJ mol⁻¹ higher than that of 9-AnCO₂•, and that the energy barriers (*E_a*) to the ipso-addi-

Table 6. Rate Constants (*k*) and Activation Parameters (*E_a* and *A*) for Disappearance of Anthroyloxyl Radicals in Acetonitrile

Radical	<i>k</i> /10 ⁶ s ⁻¹ a)	<i>E_a</i> /kJ mol ⁻¹	log (<i>A</i> /s ⁻¹)
1-AnCO ₂ •	0.10	12	7.3
2-AnCO ₂ •	0.07	17	8.0
9-AnCO ₂ •	0.15	23	9.2
1-NpCO ₂ • ^{b)}	0.42	31	11.1
2-NpCO ₂ • ^{b)}	2.1	32	11.7
PhCO ₂ • ^{c)}	4.5	31	12.1

a) At ambient temperature. b) Ref. 18. c) Ref. 2.

tion and decarboxylation of 9-AnCO₂• are 55.6 and 96.7 kJ mol⁻¹, respectively.²⁵ In the transition state of the ipso-addition, the distance between the ipso-carbon and the oxygen radical center is 175.7 pm, while the C_{ipso}-C_α bond length is 189.6 pm in the transition state of the decarboxylation. These results are in keeping with the experimental results that 9-AnCO₂• undergoes ipso-addition but not decarboxylation (cf. Subsection 6).

The endothermicity in peroxy-radical formation (addition to molecular oxygen) was estimated for some related radicals by UHF/PM3. Calculations predicted that the oxygen adduct of the α-lactonic radical is 41.4 kJ mol⁻¹ higher in energy than the α-lactonic radical itself (plus a triplet oxygen molecule). In the case of the oxygen-sensitive 9,10-dihydro-9-anthryl radical, its oxygen adduct is at a level 38.8 kJ mol⁻¹ higher than the parent radical. Similar calculations for a 9-phenyl-9-fluorenyl radical, which has been reported to be unreactive towards molecular oxygen,²⁴ predicted that the energy of its oxygen adduct would be 53.0 kJ mol⁻¹ higher than that of the parent radical. These results suggest that the endothermicity may be one of the factors suppressing the radical reaction with molecular oxygen; however, in the case of the α-lactonic radical the magnitude of the endothermicity is similar to that of the oxygen-sensitive 9,10-dihydro-9-anthryl radical. Consequently, the lack of oxygen-sensitivity in the α-lactonic radical can be ascribed to the exothermal elimination reverting to the aroyloxyl radical, which is unreactive towards molecular oxygen.

6. Reactivity of Anthroyloxyl Radicals. The activation parameters for disappearance of 1-, 2-, and 9-anthroyloxyl radicals were determined by monitoring their absorption spectra at 720 (for 1AFA and 2AFA) or 680 nm (for 9AFA) on 308-nm laser photolysis of AFAs in acetonitrile in the temperature range of 6.5–46 °C. The results are summarized in Table 6. In this Table the data for naphthoyloxyl (NpCO₂•) and benzoyloxyl radicals (PhCO₂•) are also listed for comparison. The activation energies of 31–32 kJ mol⁻¹ for benzoyloxyl and naphthoyloxyl radicals correspond to their decarboxylation; however, those for 1- and 2-anthroyloxyl radicals are rather small (12–17 kJ mol⁻¹) and are assigned to their hydrogen-atom abstraction by comparison with those for *o*-iodobenzoyloxyl (11 kJ mol⁻¹; log(*A*/s⁻¹) = 8.5)¹⁷ and *o*-methybenzoyloxyl radicals (17 kJ mol⁻¹; log(*A*/s⁻¹) = 10.5)²⁶ which disappear through the intermolecular and intramolecular hydrogen-atom abstraction, respectively. The intermediate *E_a* value for 9-anthroyloxyl radicals does not seem to correspond to either of these processes, but seems to be consistent with the ipso-addi-

Table 7. Rate Constants ($k_2/10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) for Reactions of Aroyloxy Radicals with Substrates in Acetonitrile

Substrate	Ar in $\text{ArCO}_2^\bullet$				
	1-An	2-An	9-An	1-Np ^{a)}	Ph ^{b)}
1,3-Cyclohexadiene	—	—	11	15400	13000
1,3-Pentadiene	—	—	2.6	610	4600
Cyclohexene	43	9.1	5.5	290	520
Cyclohexane	3.3	1.4	0.1	3.5	370
Styrene	2.2	1.1	0.3	—	70

a) Ref. 18. b) Ref. 26.

tion. The $\Delta G^\ddagger$ values estimated from the above activation parameters are in the range of 43–45 kJ mol^{-1} at 25 °C for all three kinds of $\text{ArCO}_2^\bullet$ radicals.

Bimolecular rate constants, k_2 , for the reactions of 1- and 2- $\text{ArCO}_2^\bullet$ as well as 9- $\text{ArCO}_2^\bullet$ with substrates were evaluated from pseudo-first-order decay rates obtained by monitoring the transient absorption at 720 or 680 nm in acetonitrile: $k_{\text{exptl}} = k_0 + k_2[\text{substrate}]$, where k_0 refers to first-order reactions by which the aroyloxy radical decays at zero substrate concentration. In Table 7 the k_2 values are compared with those of benzoyloxy²⁷ and 1-naphthoyloxy radicals.¹⁸ None of the three kinds of $\text{ArCO}_2^\bullet$ radicals undergo decarboxylation at ambient temperature, and they are much less reactive in hydrogen-atom abstraction and addition to olefins. These results indicate that the reactivity of the aroyloxy radicals is decreased by expansion of the conjugate ring system even if the conjugation is insufficient as seen in 9- $\text{ArCO}_2^\bullet$ with a heavily twisted geometry.

Benzoyloxy radicals have been reported to photochemically decarboxylate.⁶ As mentioned above, 9-anthroyloxy radicals were found to decarboxylate with 308 and 580 nm light. 1-Anthroyloxy and 2-anthroyloxy radicals also decarboxylated with 308 nm light; however, the efficiency seems to be lower than 9-anthroyloxy radicals (Table 5).

Conclusion

The excitation of AFAs in either the fluorenylidene or anthroate moiety results in the N–O bond cleavage to give the iminyl and the anthroyloxy radicals; the former dimerize to give 9-fluorenone azine and the latter undergo hydrogen-atom abstraction from the solvent acetonitrile to give the anthroic acids. The photocleavage of 9AFA takes place from the excited singlet state but not from the excited triplet state. The quantum yield for the bond cleavage is higher in acetonitrile than in benzene independently of the excitation wavelengths. In acetonitrile the lowest excited singlet state is attributed to the fluorenylidene moiety, and is responsible for the N–O cleavage. In benzene the excited singlet state of the fluorenylidene moiety is almost the same in energy as that of the anthroate moiety. Similar mechanisms are operative in the photocleavage of 1AFA and 2AFA.

Dynamic behavior of the anthroyloxy radicals was directly observed for the first time by means of the transient absorption method. The anthroyloxy radicals are much longer-lived than the benzoyloxy and naphthoyloxy radicals. None of the three kinds of $\text{ArCO}_2^\bullet$ radicals undergoes decarboxylation at ambient temperature, and each is much less reactive than the ben-

zoyloxy and naphthoyloxy radicals in hydrogen-atom abstraction and addition to olefins. This means that the reactivity of the aroyloxy radicals is decreased by expansion of the conjugate ring system even if the conjugation is inhibited by a heavily twisted geometry.

The 9- $\text{ArCO}_2^\bullet$ radicals are supposed to undergo the intramolecular ipso-addition and to be in addition-elimination equilibrium with the formed oxiran-2-one-3-spiro-9'-(9',10'-dihydroanthracen)-10'-yl radical. This equilibrium is not affected in the presence of molecular oxygen, but is shifted to the 9- $\text{ArCO}_2^\bullet$ side by its photoinduced decarboxylation.

Experimental

General. Proton and carbon 13 NMR spectra were recorded on a Varian Gemini-200 (200 and 50 MHz, respectively) or a JEOL FX-270 (270 and 67.5 MHz, respectively) spectrometer. UV absorption and fluorescence spectra were measured on a JASCO Ubest 55 or a Shimadzu 1600 spectrophotometer and a Hitachi F-4000 spectrofluorimeter, respectively. Elemental analyses were performed at the Analysis Center of the University of Tsukuba.

Materials. Solvents, acetonitrile and benzene (Dojin, spectrograde) were used as received. 9-Anthroic acid was commercially available (Aldrich). 2-Anthroic acid was prepared according to a reference procedure from anthraquinone-2-carboxylic acid,²⁸ and 1-anthroic acid was also prepared according to reference procedures from benzanthrone via anthraquinone-1-carboxylic acid.^{28,29} 1-Methoxycarbonylanthracene (1MA) and 2-methoxycarbonylanthracene (2MA) were obtained by esterification of the corresponding acid in methanol in the presence of sulfuric acid. 9-Methoxycarbonylanthracene (9MA) was prepared by dehydration from 9-anthroic acid and methanol with dicyclohexylcarbodiimide (DCC) in the presence of 4-(dimethylamino)pyridine (DMAP) in dichloromethane. *N*-Methoxy-9-fluorenylideneamine (MFA) was prepared from the reaction of 9-fluorenone and methoxyamine hydrochloride in alkaline aqueous ethanol.

***N*-(9-Anthroyloxy)-9-fluorenylideneamine (9AFA).** *N*-(9-Anthroyloxy)-9-fluorenylideneamine was prepared by dehydration from 9-anthroic acid (2.22 g, 10 mmol) and 9-fluorenone oxime (2.34 g, 12 mmol) with DCC (3.1 g, 15 mmol) in the presence of DMAP (122 mg, 1 mmol) in dichloromethane (200 ml). 9AFA was purified by silica-gel column chromatography (ethyl acetate/hexane (1:10)), followed by crystallization from ethanol (1.5 g, 38%); mp 169 °C; UV (CH_3CN) λ_{max} 301 nm (ϵ 11300), 365 (9700), 385 (8800); UV (PhH) λ_{max} 304 nm (ϵ 10700), 367 (9800), 387 (9000); ^1H NMR (CDCl_3) δ 6.84–6.92 (m, 1H), 7.24–7.58 (m, 9H), 7.77 (d, 1H, J = 8 Hz), 8.02–8.09 (m, 3H), 8.24–8.30 (m, 2H), 8.62 (s, 1H); ^{13}C NMR (CDCl_3) δ 120.2, 123.6,

125.2, 125.7, 128.5, 128.7, 129.2, 130.0, 130.37, 130.43, 131.0, 131.9, 132.7, 134.3, 141.3, 142.6, 159.4, 166.6; Found: C, 83.90; H, 4.27; N, 3.50%; Calcd for $C_{28}H_{17}NO_2$: C, 84.19; H, 4.29; N, 3.51%.

***N*-(1-Anthroyloxy)-9-fluorenylideneamine (1AFA) and *N*-(2-Anthroyloxy)-9-fluorenylideneamine (2AFA).** *N*-(1-Anthroyloxy)-9-fluorenylideneamine and *N*-(2-anthroyloxy)-9-fluorenylideneamine were similarly prepared by dehydration from the corresponding anthroic acid and 9-fluorenone oxime with DCC in the presence of DMAP in dichloromethane (83 and 76%, respectively).

1AFA: mp 156–157 °C (EtOH); UV (CH_3CN) λ_{max} 301 nm (ϵ 13900), 384 (7500); UV (PhH) λ_{max} 304 nm (ϵ 13200), 387 (7500); 1H NMR ($CDCl_3$) δ 7.16–7.64 (m, 9H), 8.00–8.11 (m, 3H), 8.21–8.34 (m, 3H), 8.51 (s, 1H), 9.52 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 120.2, 120.4, 123.6, 123.7, 125.3, 126.0, 126.3, 126.4, 127.3, 127.8, 128.4, 128.5, 128.6, 129.1, 130.1, 130.4, 131.7, 131.8, 132.6, 132.8, 134.5, 134.6, 141.2, 142.7, 158.9, 164.9; Found: C, 84.10, H, 4.27, N 3.50%. Calcd for $C_{28}H_{17}NO_2$: C, 84.19; H, 4.29; N, 3.51%.

2AFA: mp 184–185 °C (EtOH); UV (CH_3CN) λ_{max} 302 nm (ϵ 26100), 383 (4600); UV (PhH) λ_{max} 302 nm (ϵ 25700), 384 (5700); 1H NMR ($CDCl_3$) δ 7.42–7.67 (m, 10H), 7.75–8.16 (m, 3H), 8.39 (d, 1H, J = 8 Hz), 8.47 (s, 1H), 8.62 (s, 1H), 8.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 120.5, 120.9, 124.0, 124.2, 126.5, 126.8, 127.3, 128.6, 128.9, 129.0, 129.4, 129.5, 130.4, 130.6, 132.2, 132.6, 133.1, 133.5, 133.8, 141.6, 143.2, 159.5, 164.8; Found: C, 84.03; H, 4.41; N, 3.44%. Calcd for $C_{28}H_{17}NO_2$: C, 84.19; H, 4.29; N, 3.51%.

***N*-(9-Anthroyloxy)diphenylmethanimine (9ADPM) and *N*-(9-Anthroyloxy)isopropylideneamine (9AIPA).** *N*-(9-Anthroyloxy)diphenylmethanimine and *N*-(9-anthroyloxy)isopropylideneamine were similarly prepared by dehydration from 9-anthroic acid and benzophenone and acetone oximes, respectively, with DCC in the presence of DMAP in dichloromethane (51 and 46%, respectively).

9ADPM: mp 151–152 °C (EtOH); 1H NMR ($CDCl_3$) δ 8.45 (s, 1H), 8.05–7.90 (m, 4H), 7.72–7.68 (m, 2H), 7.49–7.26 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 124.5, 124.8, 126.4, 127.6, 127.9, 128.2, 128.3, 128.6, 129.0, 129.2, 130.3, 130.5, 131.9, 134.0, 166.2, 166.5; Found: C, 83.51; H, 4.81; N, 3.46%. Calcd for $C_{28}H_{19}NO_2$: C, 83.77; H, 4.77; N, 3.49%.

9AIPA: mp 170 °C (EtOH); 1H NMR ($CDCl_3$) δ 1.97 (s, 3H), 2.18 (s, 3H), 7.45–7.59 (m, 4H), 8.02 (d, 2H, J = 8 Hz); 8.15 (d, 2H, J = 8 Hz), 8.54 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.8, 21.6, 124.5, 125.0, 125.6, 126.6, 128.0, 128.3, 129.1, 130.3, 164.8, 166.5; Found: C, 77.90; H, 5.52; N, 4.97%. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05%.

***N*-(*p*-Methoxybenzoyloxy)diphenylmethanimine (MeOB-DPM).** *N*-(*p*-Methoxybenzoyloxy)diphenylmethanimine was prepared from *p*-methoxybenzoyl chloride and benzophenone oxime in pyridine. MeOB-DPM was crystallized from ethanol; mp 153–154.5 °C; 1H NMR ($CDCl_3$) δ 3.81 (s, 3H), 6.82–6.85 (m, 2H), 7.36–7.77 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 55.4, 113.7, 121.0, 128.2, 128.3, 128.5, 128.8, 129.0, 129.5, 130.8, 131.4, 131.6, 132.9, 134.7, 163.4, 163.5, 165.0; Found: C, 76.06; H, 5.13; N, 4.19%. Calcd for $C_{21}H_{17}NO_3$: C, 76.12; H, 5.17; N, 4.23%.

1-(9-Anthroyloxy)-2-pyridone (9APy). 1-(9-Anthroyloxy)-2-pyridone was prepared by dehydration from 9-anthroic acid (1.38 g, 6.22 mmol) and 2-hydroxypyridine *N*-oxide (0.83 g, 7.46 mmol) with DCC (2.55 g, 12.4 mmol) in the presence of DMAP (76 mg, 0.62 mmol) in dichloromethane; 9APy was purified by

silica-gel column chromatography (ethyl acetate/hexane (1:5)) followed by crystallization from ethanol (1.4 g, 72%); mp 171–172 °C; UV (CH_3CN) λ_{max} 301 nm (ϵ 4600), 366 (7700), 386 (6800); 1H NMR ($CDCl_3$) δ 6.33 (t, 1H, J = 8 Hz), 6.91 (d, 1H, J 10 Hz), 7.45–7.71 (m, 6H), 8.08 (d, 2H, J = 8 Hz), 8.61–8.66 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 105.0, 121.1, 122.7, 124.5, 125.3, 127.5, 128.1, 129.2, 130.1, 131.0, 134.0, 134.8, 139.0, 156.9, 164.8; Found: C, 76.06; H, 4.27; N, 4.45%. Calcd for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.16; N, 4.44%.

1-(1-Anthroyloxy)-2-pyridone (1APy) and 1-(2-Anthroyloxy)-2-pyridone (2APy). 1-(1-Anthroyloxy)-2-pyridone and 1-(2-anthroyloxy)-2-pyridone were similarly prepared by dehydration from the corresponding anthroic acid and 2-hydroxypyridine *N*-oxide with DCC in the presence of DMAP in dichloromethane (78 and 82%, respectively).

1APy: mp 186–187 °C; UV (CH_3CN) λ_{max} 387 nm (ϵ 6200); 1H NMR ($CDCl_3$) δ 6.29 (t, 1H, J = 8 Hz), 6.85 (d, 1H, J = 10 Hz), 7.41–7.59 (m, 5H), 7.99–8.08 (m, 2H), 8.31 (d, 2H, J = 8 Hz), 8.50 (s, 1H), 8.62 (d, 1H, J = 10 Hz), 9.53 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 162.8, 157.0, 138.9, 135.7, 135.3, 132.5, 132.3, 131.1, 130.9, 128.5, 127.8, 127.3, 127.0, 125.9, 125.8, 124.3, 122.9, 122.5, 121.2, 104.6; Found: C, 76.08; H, 4.22; N, 4.29%. Calcd for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.16; N, 4.44%.

2APy: mp 213–214 °C; UV (CH_3CN) λ_{max} 387 nm (ϵ 3000); 1H NMR ($DMSO-d_6$) δ 6.39 (t, 1H, J = 8 Hz), 6.70 (d, 1H, J = 10 Hz), 7.54–7.68 (m, 3H), 7.98 (d, 1H, J = 8 Hz), 8.13–8.31 (m, 4H), 8.72 (s, 1H), 8.99 (s, 1H), 9.09 (s, 1H); ^{13}C NMR ($DMSO-d_6$) δ 162.9, 156.4, 140.6, 137.4, 133.9, 133.3, 132.4, 131.8, 129.6, 128.6, 128.3, 127.5, 126.6, 123.2, 122.3, 121.6, 105.2; Found: C, 75.98; H, 4.21; N, 4.31%. Calcd for $C_{20}H_{13}NO_3$: C, 76.18; H, 4.16; N, 4.44%.

Photolyses of AFAs and APys. A solution of a radical precursor in acetonitrile or benzene was irradiated with 300-nm light (Rayonet RPR-3000 lamps) or 365-nm light (Riko 400-W high-pressure mercury lamp with a $CuSO_4$ solution filter), and the products were analyzed qualitatively and quantitatively by HPLC.

Quantum Yield Measurements. The quantum yields were determined by irradiating solutions of AFAs in acetonitrile and benzene with 302- or 365-nm light from a Bunkokeiki SM-5 super-monochro-irradiator equipped with a 300-W xenon lamp. Consumption of AFAs was monitored by HPLC, and the amount of light quanta was determined by potassium tris(oxalato)ferate(III) actinometry.³⁰

Fluorescence Measurements. Fluorescence quantum yields were determined by using anthracene as a standard (ϕ_f = 0.27 in ethanol).³¹ Fluorescence lifetimes were measured by a single photon counting technique (Horiba NAES 110 time-resolved fluorophotometer).

Laser-Flash Photolyses. Laser-flash photolyses were performed by using an excimer laser (Lambda Physik LPX-100, XeCl, 308 nm, 10-ns fwhm, 70 mJ/pulse) and a pulsed xenon arc (Ushio UXL-159, 150 W) as a monitoring light source. The details of the apparatus for laser-flash photolysis have been described elsewhere.³² The temperature of each sample cell was controlled with a thermostated cell holder and a circulating water bath (Haake F3-K). An excimer laser-pumped dye laser (Lambda Physik FL3002) was used to obtain 360- (10-ns fwhm, 7–8 mJ/pulse) and 444-nm laser pulses (10-ns fwhm, 12–13 mJ/pulse) with DMQ and Coumarin 120 dyes, respectively. In two-color laser photolyses, 580-nm laser pulses were supplied from an excimer laser (Lambda Physik Lextra, XeCl, 308 nm)-pumped dye laser (Lambda Physik Scanmate; dye: Rhodamine 6G, 10-ns fwhm,

10 mJ/pulse).

MO Calculations. Semiempirical (UHF/PM3) calculations were performed to determine the optimized geometries of anthroxyloxy and other radicals and to elucidate the potential energy curves for decarboxylation and ipso-addition of 9-anthroxyloxy radicals using a program of WinMOPAC V2.0.³³ In each transition state for the ipso-addition and decarboxylation, only one imaginary frequency was calculated. The eigen vectors with the imaginary frequency mainly involve the approach of the oxygen radical center to the ipso-carbon and the elimination of the CO₂ group from the ipso-carbon, respectively. Density functional theory (DFT; UB3LYP/6-31G*) calculations were performed to determine the optimized geometries of anthroxyloxy radicals using the Gaussian 98 program.³⁴ All calculations were carried out on a Gateway Japan G6-400 personal computer.

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