J. Phys. Chem. A **1998,** *102,* 3018−3024

ARTICLES

Photophysical Properties of Intramolecular Charge-Transfer Excited Singlet State of Aminofluorenone Derivatives

Tomoyuki Yatsuhashi,[1] Yuka Nakajima, Tetsuya Shimada, and Haruo Inoue*,[2]

Department of Applied Chemistry, Graduate Course of Engineering, Tokyo Metropolitan University, 1-1 Minami-ohsawa, Hachioji, Tokyo 192-0397, Japan

Received: November 11, 1997; In Final Form: February 20, 1998

Photophysical properties of fluorenone and 12 aminofluorenone derivatives were investigated systematically by fluorescence quantum yield and picosecond lifetime measurements in cyclohexane, benzene, acetonitrile, and ethanol. Aminofluorenones underwent efficient deactivation in ethanol, except for the 1-aminofluorenone derivatives. An appreciable deuterium isotope effect on the radiationless deactivation (k_{nr}) was observed in all aminofluorenones. The largest effect was observed for 4-aminofluorenone (k_{nr}(EtOH)/k_{nr}(EtOD) = 1.9), while the smallest was for 1-aminofluorenone (k_{nr}(EtOH)/k_{nr}(EtOD) = 1.2). The radiationless deactivation in ethanol was concluded to be induced through an intermolecular hydrogen bond between the hydroxyl hydrogen of ethanol and the carbonyl oxygen of aminofluorenones. The possibility of a twisted intramolecular charge-transfer state in the case of 1-(dimethylamino)fluorenone was explored by semiempirical molecular orbital calculation.

Introduction

Solvent relaxation dynamics have attracted much attention in various systems from viewpoints of both dielectric theory and ultrafast measurements.[3] Molecules having charge-transfer excited states have been used for examining dielectric relaxation processes.[4] We have reported the photophysical properties of aminoanthraquinones (AAQs) having an amino group as the electron-donating part and carbonyl groups as electron-accepting parts.[5] The lowest excited state is an intramolecular charge-transfer state, where the negative charge is localized mainly on the carbonyl oxygen and behaves as a strong hydrogen-bond acceptor. We have also reported that intermolecular hydrogen bonding between a carbonyl group of AAQ and the hydroxyl group of the alcohol acted as an efficient radiationless deactivation mode.[6] The intermolecular hydrogen bond acts as an effective accepting mode of radiationless deactivation. The hydrogen-bonding mode has much advantage in radiationless deactivation by virtue of a large Franck−Condon factor owing to its high frequency. This finding was supported by many other researchers.[7] Though the finding was very interesting and suggestive, the AAQ results still left some ambiguity from the viewpoint of specific solvation through hydrogen bonding, since the AAQs have two carbonyls within the molecule. Aminofluorenone derivatives that have structures similar to that of AAQ but with only one carbonyl group as a hydrogen-bonding site are more suitable for examining the deactivation caused by the specific solvation. The photophysical properties of fluorenone itself have been well studied.[8] Very recently, the extensive study on the fluorescence quenching of fluorenone by alcohol was reported by Biczók et al.[9] However, those of amino-substituted fluorenones except for 1- and 3-aminofluorenone[10] have not yet been studied systematically. In this work, the photophysical properties of 12 aminofluorenones, (methylamino)fluorenones, and (dimethylamino)fluorenones were systematically studied.

Experimental Section

Materials. 9-Fluorenone and aminofluorenone derivatives, 1-amino- (1AF), 2-amino- (2AF), 3-amino- (3AF), and 4-amino-9-fluorenone (4AF) were purchased from Aldrich or Nacarai (2AF) and purified by repeated recrystallization with heptane and methanol (1AF, 3AF, and 4AF) or ethanol (fluorenone and 2AF). 2-(Dimethylamino)-9-fluorenone (2DMAF, Aldrich) was purified by column chromatography (silica gel/benzene) and repeated recrystallization with heptane. 1-(Dimethylamino)-9-fluorenone (1DMAF), 3-(dimethylamino)-9-fluorenone (3DMAF), 4-(dimethylamino)-9-fluorenone (4DMAF), 1-(methylamino)-9-fluorenone (1MAF), 2-(methylamino)-9-fluorenone (2MAF), and 4-(methylamino)-9-fluorenone (4MAF) were all synthesized by methylation of the parent aminofluorenones as reported for the synthesis of (dialkylamino)-9,10-anthraquinone.[11] They were purified by column chromatography (silica gel/benzene) and recrystallized from hexane or HPLC (ODS column, acetonitrile). 3-(Methylamino)-9-fluorenone (3MAF) was synthesized as follows: The amino group of 3AF was protected by treatment with di-*tert*-butyl dicarbonate and KOH in DMF. The product was extracted with ether and reprecipitated in water, dried, and then treated with NaH/CH_3I in THF. The methylated product was separated by column chromatography (silica gel/benzene/methanol), and the protecting group was removed by treating in concentrated H_2SO_4, extracted by ether, and reprecipitated in hexane/THF mixtures followed by recrystallization with hexane/benzene mixtures. The identification of MAFs and

S1089-5639(98)00158-3 CCC: $15.00

DMAFs was carried out using NMR, mass, and IR spectra. The purity of all the derivatives was confirmed by HPLC (ODS column, acetonitrile elution, 220 nm detection) and TLC (silica gel). Ethanol-*O-d* (Aldrich, 99.5+% D) was used as received. Benzene and ethanol were purified as described previously.[6] Cyclohexane was washed with concentrated sulfuric acid, then with water, dilute aqueous sodium carbonate, and water followed by drying with calcium chloride. It was further refluxed over calcium hydride and fractionally distilled under nitrogen. Acetonitrile was dried by refluxing over phosphorus pentoxide, distilled twice, then refluxed over sodium bicarbonate, and distilled under nitrogen.

1-(Methylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 2.93 (d, 5.1 Hz, 3 H), 6.67 (d, 8.5 Hz, 1 H), 6.95 (d, 6.8 Hz, 1 H), 7.08 (q, 4.6 Hz, 1 H), 7.33 (td, 7.4 Hz, 1 Hz, 1 H), 7.38 (dd, 7.1 Hz, 8.6 Hz, 1 H), 7.49−7.53 (m, 2 H), 7.68 (d, 7.9 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 28.9, 108.5, 112.8, 112.9, 120.7, 122.5, 128.8, 133.6, 134.4, 137.1, 142.4, 143.9, 148.9, 193.2; FAB MS m/z 210 ($M^+ + 1$); mp 123.5−125.5 °C; IR (KBr) 1672 cm^{-1}.

1-(Dimethylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 3.02 (s, 6 H), 6.88 (dd, 8.5 Hz, 0.8 Hz, 1 H), 7.16 (dd, 7.1 Hz, 0.7 Hz, 1 H), 7.34 (td, 7.3 Hz, 1.0 Hz, 1 H), 7.40 (dd, 8.6 Hz, 7.3 Hz, 1 H), 7.50−7.54 (m, 2 H), 7.71 (dt, 7.7 Hz, 0.7 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 42.9, 110.9, 117.4, 118.1, 120.2, 122.6, 128.9, 133.5, 134.2, 135.7, 142.3, 145.7, 151.2, 189.9; FAB MS m/z 224 ($M^+ + 1$); mp 75.3−75.5 °C; IR (KBr) 1688 cm^{-1}.

2-(Methylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 2.74 (d, 4.9 Hz, 3 H), 6.21 (q, 5.1 Hz, 1 H), 6.65 (dd, 2.4 Hz, 8.0 Hz, 1 H), 6.78 (d, 2.2 Hz, 1 H), 7.13 (td, 7.1 Hz, 1.7 Hz, 1 H), 7.43−7.49 (m, 4 H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 29.6, 107.2, 116.0, 119.1, 121.9, 123.5, 126.6, 130.5, 133.0, 134.9, 135.2, 145.8, 151.1, 194.0; FAB MS m/z 210 ($M^+ + 1$); mp 162.5−163.0 °C; IR (KBr) 1703 cm^{-1}.

3-(Methylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 2.84 (d, 4.9 Hz, 3 H), 6.40 (dd, 8.3 Hz, 2.0 Hz, 1 H), 6.89 (d, 2.0 Hz, 1 H), 7.01 (q, 4.9 Hz, 1 H), 7.32 (td, 7.4 Hz, 1.0 Hz, 1 H), 7.36 (d, 8.3 Hz, 1 H), 7.46 (dt, 7.3 Hz, 0.7 Hz, 1 H), 7.50 (td, 7.5 Hz, 1.2 Hz, 1 H), 7.66 (d, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 28.7, 120.2, 120.5, 122.4, 126.2, 129.0, 133.4, 135.8, 142.7, 146.6, 155.9, 190.3; FAB MS m/z 210 ($M^+ + 1$); mp 122.5−123.5 °C; IR (KBr) 1678 cm^{-1}.

3-(Dimethylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 3.12 (s, 6 H), 6.54 (dd, 8.5 Hz, 2.4 Hz, 1 H), 7.12 (d, 2.4 Hz, 1 H), 7.33 (td, 7.4 Hz, 1.0 Hz, 1 H), 7.42 (d, 8.3 Hz, 1 H), 7.48 (dt, 7.3 Hz, 1 Hz, 1 H), 7.52 (td, 5.0 Hz, 1.0 Hz, 1 H), 7.77 (dt, 7.3 Hz, 1 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 40.0, 104.0, 110.3, 120.4, 120.4, 122.4, 125.8, 129.0, 133.5, 135.7, 142.9, 146.2, 155.2, 190.5; FAB MS m/z 224 ($M^+ + 1$); mp 181.5−182.0 °C; IR (KBr) 1678 cm^{-1}.

4-(Methylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 2.87 (d, 5.1 Hz, 3 H), 4.64 (q, 4.6 Hz, 1 H), 6.89 (d, 8.3 Hz, 1 H), 6.94 (dd, 7.1 Hz, 0.8 Hz, 1 H), 7.23 (t, 7.7 Hz, 1 H), 7.26 (td, 7.5 Hz, 0.8 Hz, 1 H), 7.54 (t, 8.2 Hz, 1 H), 7.55 (d, 6.4 Hz, 1 H), 7.88 (d, 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 30.1, 111.9, 118.3, 122.4, 123.5, 125.6, 127.1, 130.5, 132.6, 134.2, 134.9, 144.1, 145.2, 193.8; FAB MS m/z 210 ($M^+ + 1$); mp 180.5−181.0 °C; IR (KBr) 1699 cm^{-1}.

4-(Dimethylamino)-9-fluorenone. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C) δ 2.78 (s, 1 H), 7.29 (dd, 6.8 Hz, 1.5 Hz, 1 H), 7.33 (t, 7.4 Hz, 1 H), 7.34 (td, 7.4 Hz, 0.8 Hz, 1 H), 7.38 (td, 7.8 Hz, 1.4 Hz), 7.60 (dt, 7.3 Hz, 1.0 Hz, 1 H), 7.62 (td, 7.6 Hz, 1.2 Hz, 1 H), 7.81 (td, 7.6 Hz, 0.8 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C) δ 43.7, 117.6, 123.5, 124.0, 125.9, 128.3, 130.3, 133.0, 134.8, 134.9, 135.2, 143.4, 150.1, 193.2; FAB MS m/z 224 ($M^+ + 1$); mp 104.0−104.5 °C; IR (KBr) 1709 cm^{-1}.

Measurements. The absorption spectra were measured with a Shimadzu UV-2100PC spectrophotometer. The steady-state fluorescence spectra were measured with a Hitachi F-4010 spectrofluorometer equipped with a Hamamatsu R928 photomultiplier tube. Instrumental response was corrected by rhodamine B in ethylene glycol and standard tungsten lamp.[12] Fluorescence quantum yields (Φ_F) were determined by comparison with quinine bisulfate in 0.5 M aqueous sulfuric acid solution ($\Phi_F = 0.546$).[13] This value as a standard was confirmed by observing that of anthracene in ethanol ($\Phi_F = 0.28$). The literature value for anthracene is 0.27.[14] A refractive index[15] correction was made for each sample. The solutions were prepared with absorbances around 0.05 for avoiding inner filter effects. The fluorescence decay and time-resolved fluorescence spectra were measured using a picosecond fluorescence lifetime measurement system under photon-counting conditions (Hamamatsu, C4334 streak scope, connected with CHROMEX 250IS polychromater) with a Hamamatsu PLP-02 semiconductor laser (420 nm, fwhm 20 ps, 1.19 mW, 1 MHz) and an EKSPLA PV-401 optical parametric generator (420−560 nm, fwhm 25 ps, >1 mJ, 5 Hz) pumped by the third harmonic radiation of a Nd^{3+} YAG laser, EKSPLA PL2143B (355 nm, 25 ps fwhm, 15 mJ), or by the third harmonic of the PL2143B itself. The laser flux was reduced with neutral density filters to avoid multiphoton absorption processes and nonlinear effects in the latter case. A single picosecond optical pulse of the PL2143B in the regenerative amplifier was extracted by an InGaAs photodiode (Hamamatsu, G3476-05) and used as a pretrigger for the streak scope. This method turned out to be very useful to avoid trigger jitter problem of the streak scope, because no additional jitter owing to this pretrigger method was involved. Fluorescence time profiles were fitted by a convolution method. All measurements were carried out under air at 296 K.

Results and Discussions

Photophysical Properties of AF, MAF, and DMAF. The monosubstituted aminofluorenone derivatives have four structural isomers, while those of AAQ have only two isomers. These four isomers could be classified into two groups of (1) 1AF and 3AF and (2) 2AF and 4AF. The former group has an amino group in the ortho or para position to the carbonyl group, and the latter has an amino group in the meta position to the carbonyl group. They have a similar infrared absorption of the carbonyl group,[16] ^{17}O NMR chemical shifts of the carbonyl oxygen,[17a] and ^{1}H NMR chemical shifts of the amino proton[18] within each group. The classification of aminofluorenones in the excited singlet state is interesting. The photophysical properties of fluorenone and 12 aminofluorenone derivatives such as aminofluorenones (AFs), (methylamino)fluorenones (MAFs), and (dimethylamino)fluorenones (DMAFs) in cyclohexane, benzene, acetonitrile, and ethanol are shown in Table 1. The radiative rate constant (k_r) and nonradiative rate constant (k_{nr}) were calculated from fluorescence quantum yield (Φ_F) and fluorescence lifetime (τ) as

$$k_r = \Phi_F/\tau \qquad k_{nr} = \tau^{-1} - k_r$$

TABLE 1: Photophysical Properties of Aminofluorenone Derivatives[a]

		absorption		fluorescence			$\Delta\nu$	E_{0-0}	k_r	k_{nr}
		λ_{max} (nm)	ϵ (10^3 M^{-1} cm^{-1})	λ_{max} (nm)	Φ_F (10^{-2})	τ (ns)	(10^3 cm^{-1})	(10^4 cm^{-1})	(10^7 s^{-1})	(10^8 s^{-1})
fluorenone	cyclohexane	382[b]	0.28	472	0.035	0.14[c]	5.0	2.37	0.25	71
	benzene	380[b]	0.30	485	0.78	2.8[c]	5.7	2.29	0.28	3.5
	acetonitrile	377[b]	0.26	514	2.3	19[c]	7.1	2.24	0.12	0.52
	ethanol	379[b]	0.26	562	0.11	0.04/2.1[d]	8.6	2.21	0.052[e]	4.8[e]
1AF	cyclohexane	407[b]	6.5	471	3.1	0.80	3.3	2.28	3.9	12
	benzene	416	6.5	482	5.5	1.4	3.3	2.21	3.9	6.7
	acetonitrile	420	6.7	501	5.7	2.3	3.9	2.16	2.5	4.1
	ethanol	431	7.8	521	6.8	0.05/4.0[d]	4.0	2.10	1.7	2.3
2AF	cyclohexane	455	0.50	569	0.86	4.0	4.4	1.97	0.22	2.5
	benzene	469	0.54	622	0.099	0.84	5.2	1.84	0.12	12
	acetonitrile[f]	481	0.54							
	ethanol[f]	488	0.79							
3AF	cyclohexane	386[b]	1.8	476[g]	0.60	0.56/2.4[h]	4.9	2.30	0.25[e]	4.1[e]
	benzene	395	2.8	504	13	11	5.5	2.19	1.2	0.79
	acetonitrile	409	4.0	544	4.3	5.9	6.1	2.08	0.73	1.6
	ethanol	429	4.7	592	0.33	0.04/0.29[d]	6.4	1.97	1.1[e]	34[e]
4AF	cyclohexane	427[b]	1.8	513[g]	3.5	3.2	3.9	2.14	1.1	3.0
	benzene	440	1.9	544	7.4	9.3	4.3	2.03	0.80	1.0
	acetonitrile	451	1.8	604	1.2	4.2	5.6	1.90	0.29	2.4
	ethanol	458	1.7	667	0.024	0.04/0.080[d]	6.8	1.86	0.30[e]	125[e]
1MAF	cyclohexane	432	7.2	497	4.2	1.6	3.0	2.14	2.6	6.0
	benzene	445	7.6	519	6.5	2.8	3.2	2.07	2.4	3.3
	acetonitrile	445	7.5	533	6.5	4.2	3.7	2.04	1.7	2.2
	ethanol	448	7.6	542	6.4	2.8	3.9	2.01	2.3	3.3
2MAF	cyclohexane	474	0.69	587	0.73	3.1	4.1	1.82	0.23	3.2
	benzene	491	0.76	635	0.10	0.63	4.6	1.77	0.17	16
	acetonitrile[f]	508	0.70							
	ethanol[f]	511	0.67							
3MAF	cyclohexane	389	4.0	489	4.5	0.79/6.5[h]	5.3	2.25	0.69[e]	1.5[e]
	benzene	409	4.9	509	19	9.4	4.8	2.15	2.0	0.86
	acetonitrile	424	5.9	548	6.4	4.3	5.3	2.05	1.5	2.2
	ethanol	436	6.5	583	0.65	0.03/0.77[d]	5.8	1.94	0.84[e]	13[e]
4MAF	cyclohexane	449[b]	2.1	536[g]	9.4	8.8	3.6	2.04	1.1	1.0
	benzene	461	2.1	570	6.3	8.4	4.1	1.93	0.75	1.1
	acetonitrile	471	2.0	638	0.51	2.2	5.6	1.81	0.23	4.5
	ethanol	477	1.8	686	0.014	0.04/0.090[d]	6.4	1.80	0.16	111
1DMAF	cyclohexane	433[b]	6.4	498	0.16	<0.01/1.3[h]	3.0	2.13	0.12[e]	7.7[e]
	benzene	445	6.8	520	0.24	0.02/2.2[h]	3.2	2.06	0.11[e]	4.5[e]
	acetonitrile	444	6.7	534	0.27	0.03/2.8[h]	3.8	2.03	0.10[e]	3.6[e]
	ethanol	449	6.6	541	0.40	0.01/2.7[h]	3.8	2.01	0.15[e]	3.7[e]
2DMAF	cyclohexane	484	0.95	600[g]	0.87	3.3	4.0	1.85	0.26	3.0
	benzene	507	0.95	644	0.12	0.79	4.2	1.72	0.15	13
	acetonitrile[f]	510	0.86							
	ethanol[f]	509	0.77							
3DMAF	cyclohexane	400[b]	5.9	491[g]	14	6.1	4.6	2.21	2.9	1.3
	benzene	420	6.8	526	23	11	4.8	2.10	2.7	0.70
	acetonitrile	431	7.4	557	8.3	4.8	5.3	2.00	2.2	1.9
	ethanol	437	7.2	592	0.81	0.04/0.70[d]	6.0	1.92	1.2[e]	14[e]
4DMAF	cyclohexane	412[b]	1.1	532	7.5	8.0	5.5	2.09	0.94	1.2
	benzene	433	1.1	575	7.3	10	5.7	1.96	0.73	0.93
	acetonitrile	439	1.1	646	0.75	4.2	7.3	1.85	0.18	2.4
	ethanol	438	1.0	700	0.027	0.04/0.12[d]	8.5	1.89	0.23[e]	83[e]

[a] ϵ, Φ_F, τ, $\Delta\nu$, E_{0-0}, k_r, and k_{nr} are molar extinction coefficient, fluorescence quantum yield, fluorescence lifetime, the difference of λ_{max} between absorption and fluorescence spectra in cm^{-1} unit, the 0−0 transition energy of excited singlet state, radiative rate constant, and nonradiative rate constant. The accuracy of data is estimated as Φ_F (±10%), τ (±10%), λ_{max} of absorption (±1 nm), λ_{max} of fluorescence (±2 nm), and λ_{max} of fluorescence of quantum yield below 10^{-3} (±3 nm). [b] Absorption spectrum shows weak vibronic structure. [c] Reference 8. [d] Fluorescence decay profile was wavelength dependent and was fitted by double-exponential decay. [e] Calculated with Φ_F and τ (longer lifetime). [f] Fluorescence was not observed. [g] Fluorescence spectrum shows two peaks with structure and the long-wavelength one was shown. [h] Fluorescence decay profile was fitted by double-exponential decay.

The 0,0 transition energy was obtained from the crossing point between the normalized absorption spectrum and the fluorescence spectrum. The $\Delta\nu$ is the difference between λ_{max} of absorption and fluorescence in cm^{-1} units. As seen in the absorption spectrum of 4MAF as a typical example in Figure 1, a new absorption band has appeared in the visible region by introducing an amino substituent into the fluorenone nucleus. Theory predicts the new absorption bands of aminofluorenones in the visible region as being due to intramolecular charge transfer from the amino moiety to the fluorenone π skeleton by analogy to AAQs.[19] The large $\Delta\nu$ values in Table 1 are in accord with this assignment. The absorption spectra had weak vibronic structure in cyclohexane but were broadened in other solvents. A Lippert−Mataga plot[20] indicated that the excited states of 4AF and 3DMAF as typical examples have very polar electronic structures. The differences of dipole moment between the excited and ground states were 5.2 D (4AF),[21] 3.8 D (3DMAF),[21] 3.5 D (1AF),[10] and 4.9 D (3AF)[10] but smaller than those of AAQs, 6.5 D (2-amino-9,10-anthraquinone, 2AAQ) and 7.3 D (2-piperidino-9,10-anthraquinone, 2PAQ).[22]

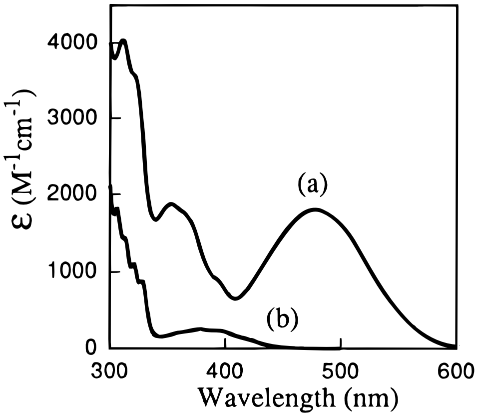

Figure 1. Absorption spectra of (a) 4-(methylamino)fluorenone and (b) fluorenone in ethanol.

The fluorescence decay profiles of aminofluorenone derivatives except 1DMAF, 3AF, and 3MAF were fairly described as a single exponential in cyclohexane, benzene, and acetonitrile, while in ethanol they were wavelength dependent and exhibited two components of the decay, except 1MAF (single component in all solvents examined) and 1DMAF (two components but weakly wavelength dependent in all solvents examined). The radiative (k_r) and nonradiative rate constants (k_{nr}) in ethanol were calculated from the longer lifetime among the two-component decays (Table 1). Obviously, 1-substituted aminofluorenones exhibited different characteristics than did the 3- and 4-substituted derivatives. The difference was most obvious in the nonradiative rate constant (k_{nr}). 1-Substituted derivatives were rather insensitive to solvent, while 3- and 4-substituted derivatives were very sensitive to solvent polarity. 2-Substituted aminofluorenones having an exceptionally small extinction coefficient for light absorption apparently showed behavior similar to those of 3- and 4-substituted fluorenones, though the rate constants in acetonitrile and ethanol could not be determined because fluorescence in these solvents was too weak even at 77 K.

1-Substituted Aminofluorenones. Moog et al. reported similar characteristics of 1AF and postulated that 1AF had an intramolecular hydrogen bond between the amino hydrogen and carbonyl oxygen acting to induce efficient internal conversion mode, which caused the insensitivity to solvent nature.[10] In ethanol, the intramolecular hydrogen bond might be replaced with an intermolecular one with ethanol to decrease the rate of internal conversion.[10] However, the methylated aminofluorenones 1MAF and 1DMAF were revealed to have characteristics similar to 1AF in the present study (Table 1). Since 1DMAF has no amino hydrogen and no intramolecular hydrogen bond is involved, the explanation of Moog et al.[10] may not necessarily be valid. Simple contradicting question also arises as to why the replaced intermolecular hydrogen bond is less effective in reducing the radiationless deactivation in contrast to the efficient deactivation caused by the intermolecular hydrogen bond in the cases of 3- and 4-substituted aminofluorenones described below. In the cases of AAQs, the intermolecular hydrogen bond was demonstrated to be much more efficient for radiationless deactivation than the intramolecular hydrogen bond between the amino hydrogen in 1-position and carbonyl oxygen.[5] The smallest deuterium isotope effect on the nonradiative process of 1AF (k_{nr}(EtOH)/k_{nr}(EtOD) = 1.2) among the aminofluorenones as described below (Table 2) also needs an explanation. Intramolecular hydrogen-bonded molecule such as 1-amino-9,10-anthraquinone (1AAQ) showed a larger deuterium isotope effect of 7.1.[5] The large difference between the two cases strongly suggests that these two molecules do not have the same deactivation mechanism through an intramolecular hydrogen bond. 1AF has too long a distance between the carbonyl group and the amino hydrogen to form a strong hydrogen bond.[17b,23] Srivatsavoy et al. reported that molecules having intersystem crossing as the dominant mode of deactivation showed small isotope effects such as those of 1-(acetylamino)-9,10-anthraquinone (1.3) and 1,5-diamino-9,10-anthraquinone (1.6), while the molecules having internal conversion as the dominant mode of deactivation showed a large isotope effect such as those of 1AAQ (8.3) and 1-(methylamino)-9,10-anthraquinone (6.5).[24] Furthermore, intramolecular hydrogen bond of 1AF in the ground state was discussed by Baumstark et al. with ^{17}O NMR; the chemical shifts of the carbonyl oxygen of 1AF were not so deshielded by the amino hydrogen compared with 3AF, and this result was significantly different from other typical intramolecular hydrogen-bonded compound such as hydroxyacetophenone[25] and 1AAQ.[17b] The intramolecular hydrogen bond of 1AF was concluded to be weak because of the long distance between the carbonyl oxygen and the amino hydrogen.[17b] Possibilities other than the simple explanation involving an intramolecular hydrogen bond should be further considered. An involvement of the twisted intramolecular charge-transfer state especially in the case of 1DMAF as described in a later section and intersystem crossing to the triplet state owing to solvent-induced energy changes may be candidates for explaining the photophysical behavior. Further study should be done to clarify the photophysical behavior of 1-substituted aminofluorenones.

TABLE 2: Photophysical Properties of Fluorenone, AF, MAF, and DMAF in Ethanol-*O-d* and Deuterium Isotope Effects on Radiative and Nonradiative Rate Constants

	Φ_f (10^{-2})	τ (ns)[a]	k_r (10^7 s^{-1})[b]	k_{nr} (10^8 s^{-1})[b]	$k_{r(EtOH)}$/ $k_{r(EtOD)}$	$k_{nr(EtOH)}$/ $k_{nr(EtOD)}$
fluorenone	0.16	0.05/4.0	0.040	2.5	1.3	1.9
1AF	8.6	0.04/4.5	1.9	2.0	0.89	1.2
3AF	0.53	0.04/0.47	1.1	21	1.0	1.6
4AF	0.039	0.04/0.15	0.26	67	1.2	1.9
1MAF	8.8	3.8	2.3	2.4	1.0	1.4
3MAF	0.97	0.04/1.0	0.97	9.9	0.87	1.3
4MAF	0.027	0.03/0.12	0.23	83	0.73	1.3
1DMAF	0.50	0.01/3.9	0.13	2.6	1.2	1.4
3DMAF	1.1	0.04/0.97	1.1	10	1.0	1.4
4DMAF	0.044	0.04/0.22	0.20	45	1.2	1.8

[a] Fluorescence decay profile was fitted by double-exponential decay. [b] The rate constant was calculated by Φ_F and τ (long one). The accuracy of data is estimated as Φ_F (±10%) and τ (±10%).

3- and 4-Substituted Aminofluorenones. In contrast to 1-substituted aminofluorenones, 3- and 4-substituted aminofluorenones exhibited a large solvent effect on radiationless deactivation (Table 1). They exhibited very efficient deactivation in ethanol. Very similar effects were also observed in AAQs.[5] Specific deactivation is supposed to operate in ethanol through specific solvation such as intermolecular hydrogen bonding, as demonstrated by the deuterium isotope effect described below (Table 2).

The two-component decay in ethanol was observed in the short wavelength region, and the corresponding rise and decay behavior was observed in the long-wavelength region. These results suggest that the fast component reflects the relaxation of the original fluorescent state (S_1) to form a relaxed excited state (S_1(RX)) and the slow component is the decay of S_1(RX). The time constant of the fast component was around 30−40 ps. This corresponds to the dielectric relaxation of ethanol.[26] Fluorescence λ_{max} of AFs and MAFs in rigid ethanol at 77 K shifted to wavelengths shorter than those in fluid ethanol at room temperature, and they were yet similar or shorter than those in benzene at room temperature.[27] These results indicated that solvent reorientation was surely involved in the fluorescence decay process. Upon the sudden appearance of a giant dipole by excitation to the intramolecular charge-transfer state, dielectric reorientation of ethanol would simultaneously lead to specific solvation such as the intermolecular hydrogen bond of hydroxyl hydrogen to the carbonyl oxygen with increased minus charge. The ratio of nonradiative rate constants in ethanol to those in benzene were 158 (2AAQ),[5] 263 (2PAQ),[5] 43 (3AF), and 125 (4AF), respectively. The result for 4AF was almost identical to that of 2AAQ, but 3AF had a smaller value. The value may partly reflect the degree of charge transfer in the excited state, supposing the nonradiative deactivation is caused by intermolecular hydrogen bonding. The strength of the hydrogen-bonding interaction should be largely dependent on the degree of minus charge on the carbonyl oxygen. The excited states of AFs, thus, are considered to have essentially weaker charge-transfer nature than AAQs. This is also supported by the smaller dipole moment difference of AFs than AAQs estimated from the Lippert−Mataga plots mentioned above.

Deuterium Isotope Effect on Radiationless Deactivation. To obtain more explicit information about the radiationless deactivation in ethanol, deuterium isotope effects were examined (Table 2). Very interestingly, in deuterated ethanol (C_2H_5OD), the radiationless deactivation (k_{nr}) was suppressed appreciably in all the aminofluorenones and fluorenone itself. 1AF had the smallest effect, while 4AF had the largest effect. 3DMAF and 4DMAF having no amino hydrogen atom showed deuterium effects similar to those of the parent 3AF and 4AF. This strongly suggests that the N−H bond of the amino group in AFs does not play an important role in the internal conversion process. The appreciable deuterium isotope effect on radiationless deactivation in ethanol clearly indicated that the process was induced through intermolecular hydrogen bonding with the hydroxyl hydrogen of ethanol. These results are in striking contrast to the case of coumarin derivatives (the deuterium isotope effect is around 1.10) which suffers only general dielectric relaxation.[28] The deuterium effect of AFs could be ascribed to a difference of the Franck−Condon factor in radiationless transition, supposing that the quantum mechanical initial state was the hydrogen-bonded state in the relaxed excited state (S_1(RX)).[29]

Methyl Substitution and TICT Possibility. The methyl substitution on the amino group significantly changed the nature of AFs. The correlation between absorption ν_{max} and the ionization potential of substituents is shown in Figure 2.[30] The data for hydroxy-9-fluorenones (HFs) are also plotted in Figure 2. The absorption λ_{max} of MAFs and DMAFs shifted to the red compared with the corresponding AFs, since introduction of a methyl group lowered the ionization potential of the amino moiety as in the case of AAQs.[31] A good correlation in Figure 2 clearly shows that the first absorption bands of AF derivatives has an intramolecular charge-transfer nature. The tendency to shift was not so dependent on substitution position but was prominent in 1-substituted fluorenones (Figure 2). In each correlation, 1DMAF and 4DMAF obviously deviated from the plot. The deviation might be correlated with their ground-state structure. We calculated the most stable structure of AF derivatives in the ground state by MOPAC93 (PM3). The optimized structures of 2DMAF and 3DMAF in the ground state were coplanar, but 4DMAF and 1DMAF could not be coplanar owing to the steric hindrance between the dimethylamino group and the hydrogen atom at the 5-position (4DMAF) or the carbonyl group (1DMAF). The most stable structures estimated by MOPAC93 (PM3) are shown in Figure 3. 4DMAF favored an almost perpendicular arrangement between the fluorenone nucleus and the substituent in the ground state, while 1DMAF had a slightly rotated dimethylamino group. This estimation was supported by NMR measurements. The chemical shift of the methyl protons of 4DMAF shifted to higher magnetic field than 4MAF in contrast to other 2- and 3-substituted derivatives. This clearly indicated that the methyl groups of 4DMAF were not coplanar with the fluorenone π skeleton and were not magnetically deshielded. Steric hindrance interrupts the conjugation between the fluorenone nucleus and the lone pair of nitrogen and charge-transfer interaction of 4DMAF becomes smaller as in the cases of aniline derivatives.[32] This is also true in 1DMAF, but the degree of steric hindrance is smaller than that of 4DMAF. The effects of structural difference on rate constants (Table 1) was not apparently observed among 4-aminofluorenone derivatives but was evident among 1-aminofluorenone derivatives. Fluorescence quantum yields and lifetimes were very varied between 1MAF and 1DMAF. The radiative rate constant (k_r) of 1DMAF was much smaller in every solvent than those of 1AF and 1MAF, while the radiationless

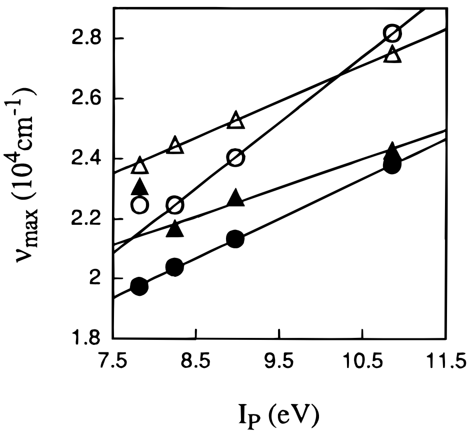

Figure 2. Correlation between ν_{max} of absorption of fluorenone derivatives and the ionization potential of the corresponding methylamine (AF), dimethylamine (MAF), trimethylamine (DMAF), and methanol (HF). (○) 1AF, 1MAF, 1DMAF, 1HF; (●) 2AF, 2MAF, 2DMAF, 2HF; (△) 3AF, 3MAF, 3DMAF, 3HF; (▲) 4AF, 4MAF, 4DMAF, 4HF.

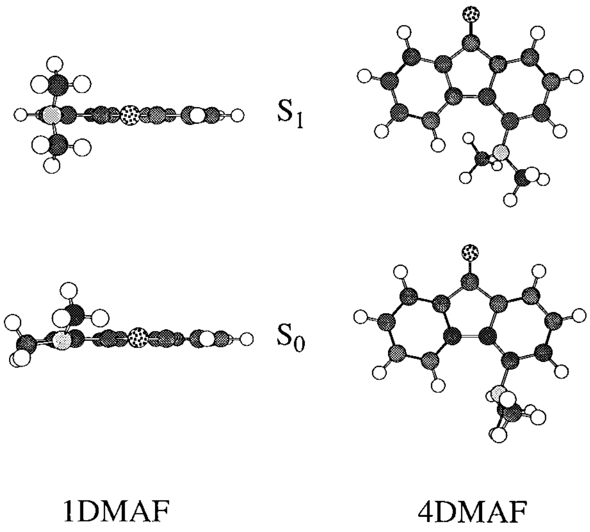

Figure 3. Most stable structure of 1DMAF (side view) and 4DMAF (top view) in the ground (S_0) and excited (S_1) state optimized by MOPAC93 (PM3).

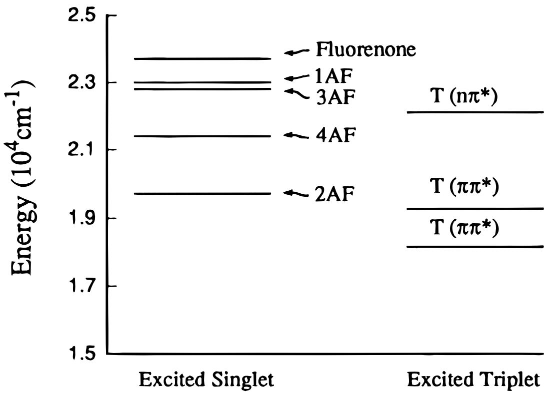

Figure 4. Energy diagram of fluorenone and S_1(CT) level of AF in cyclohexane. The triplet energy of fluorenone was referred from: Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429.

deactivation (k_{nr}) was similar for 1DMAF, 1AF, and 1MAF. This indicated that the nature of the relaxed excited state (S_1-(RX)) of 1DMAF was quite different from those of other derivatives. The fluorescence decay profiles of 1DMAF showed a small wavelength dependence with a clear two-component decay in all solvents examined. The very short decay within 20 ps was the main contributor. Thus, the original fluorescent state of 1DMAF immediately relaxed to a weakly fluorescent one. For other 3- and 4-substituted derivatives, such a striking difference between MAF and DMAF were not found. When molecules having charge-transfer excited states were substituted by dimethylamino substituents instead of amino groups, formation of TICT (twisted intramolecular charge transfer) states was observed in some cases.[33] TICT formation in structurally similar compounds such as 2-(dimethylamino)-9,10-anthraquinone[34] and 4-(dimethylamino)phthalimide was also reported.[35] We have compared the possibility of TICT states by semiempirical molecular orbital calculation. The calculation was done by MOPAC93 (PM3) and the most stable conformation was estimated in the excited and ground state. All the AFs and MAFs always favored coplanar conformation. Only 1DMAF, however, favored the perpendicular form in the S_1 state (Figure 3). The energy stabilization by transformation from the Franck−Condon state of 1DMAF to the fully optimized perpendicularly relaxed conformer was calculated as 0.17 eV. The calculation may support the experimental result that 1DMAF also showed a two-component decay even in cyclohexane as in the TICT case of *N*-phenylnaphthalimide derivatives.[36] 4DMAF was another special case that had already the perpendicular form in the ground state owing to the strong repulsion between the dimethylamino group and the hydrogen on the opposite phenyl ring (Figure 3). Though appreciable structural change in the excited state of 4DMAF was predicted by calculation, a striking difference was not found experimentally among 4AF, 4MAF, and 4DMAF (Table 1). The already perpendicular form in Franck−Condon excited state of 4DMAF would lead to an ordinal internal conversion to the ground state. As discussed above, only 1DMAF had a possibility of TICT formation. Further study on the TICT possibility is now under progress by both experiment and theoretical calculation.

Energy State Diagram of Aminofluorenones. The 0,0 transition energies of fluorenone, 1AF, 2AF, 3AF, and 4AF in cyclohexane observed in this study are simply plotted on the energy diagram of Figure 4. The diagram contains the excited triplet states of fluorenone estimated by Nagakura et al.[8a] The assignment of the lowest excited singlet state of fluorenone has been discussed by many researchers.[8] In nonpolar solvent, n,π^*, and π,π^* states are in close proximity. In cyclohexane, the lowest excited singlet state was assigned to n, π^*,[8a] while it was fairly assigned to π,π^* in benzene and in polar solvents.[8b,c] As easily anticipated, energy state diagrams of 1AF, 3AF, and even 4AF would be complicated owing to the close lying n,π^* state, while 2AF may not be so much affected by the n,π^* state. Mixing with n,π^* and the relative positioning against the n, π^* and π,π^* triplet states in each solvent would largely affect the photophysical properties. Though detailed energy diagrams are not simply obtained here, the larger deactivation in cyclohexane than in benzene observed in all the aminofluorenones except the 2-substituted derivatives (Table 1) well characterizes the delicate positioning against the triplet states. Detailed study in each case such as temperature effect on fluorescence intensity and triplet yield[8c] would also be as meaningful as the fundamental data in Table 1 and theoretical study for the further understanding of energy state diagram.

Conclusion

The photophysical properties of aminofluorenones were revealed to be strongly dependent on its substituted position by examining 12 derivatives systematically. The nonradiative deactivation of all AFs except 1-aminofluorenone derivatives were substantial in ethanol as in the case of AAQs. Intramolecular charge-transfer excited states of AFs were effectively quenched through intermolecular hydrogen bond between carbonyl oxygen of AFs and hydroxyl hydrogen of ethanol. The possibility of TICT was found only in 1DMAF by experiment and with theoretical calculation.

Acknowledgment. We thank Dr. Jonas Kolenda of Tokyo Instruments Inc. and Mr. Haruhisa Saito of Hamamatsu Photonics K. K. for their kind contribution to our laser system. This work was partly defrayed by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References and Notes

(1) Present address: Department of Chemistry, Faculty of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan.

(2) To whom correspondence should be addressed. E-mail: inoue-haruo@c.metro-u.ac.jp.

(3) Bagchi, B. *Annu. Rev. Phys. Chem.* **1989**, *40*, 115. Simon, J. D. *Pure Appl. Chem.* **1990**, *62*, 2243.

(4) Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311. Reid, P. J.; Barbara, P. F. *J. Phys. Chem.* **1995**, *99*, 3554. Stratt, R. M.; Maroncelli, M. *J. Phys. Chem.* **1996**, *100*, 12981.

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

(6) Yatsuhashi, T.; Inoue, H. *J. Phys. Chem. A* **1997**, *101*, 8166.

(7) (a) Ritter, J.; Borst, H. U.; Lindner, T.; Hauser, M.; Brosig, S.; Bredereck, K.; Steiner, U. E.; Kühn, D.; Kelemen, J.; Kramer., H. E. A. *J. Photochem. Photobiol. A* **1988**, *41*, 227. Borst, H. U.; Kelemen, J.; Fabian, J.; Nepras, M.; Kramer, H. E. A. *J. Photochem. Photobiol. A* **1992**, *69*, 97. (b) Srivatsavoy, V. J. P.; Venkataraman, B.; Periasamy, N. *J. Photochem. Photobiol. A* **1992**, *68*, 169. *Proc. Indian Acad. Sci. Chem. Sci.* **1992**, *104*, 731. (c) Flom, S. R.; Barbara, P. F. *J. Phys. Chem.* **1985**, *89*, 4489. (d) Jones, G., II; Feng, Z.; Bergmark, W. R. *J. Phys. Chem.* **1994**, *98*, 4511. (e) Lin, S.; Struve, W. S. *J. Phys. Chem.* **1991**, *95*, 2251.

(8) (a) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429. Andrews, L. J.; Deroulede, A.; Linschitz, H. *J. Phys. Chem.* **1978**, *82*, 2304. Biczók, L.; Bérces, T. *J. Phys. Chem.* **1988**, *92*, 3842. Fujii, T.; Sano, M.; Mishima, S.; Hiratsuka, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1833. (b) Kuboyama, A. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1540. Yoshihara, K.; Kearns, D. R. *J. Chem. Phys.* **1966**, *45*, 1991. Singer, L. A. *Chem. Phys. Lett.* **1969**, *12*, 923. (c) Biczók, L.; Bérces, T.; Márta, F. *J. Phys. Chem.* **1993**, *97*, 8895.

(9) Biczók, L.; Bérces, T.; Linschitz, H. *J. Am. Chem. Soc.* **1997**, *119*, 11071.

(10) Moog, R. S.; Burozski, N. A.; Desai, M. M.; Good, W. R.; Silvers, C. D.; Thompson, P. A.; Simon, J. D. *J. Phys. Chem.* **1991**, *95*, 8466.

(11) Arai, S.; Kato, S.; Hida, M. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1458.

(12) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Essex, 1968; Chapter 3.

(13) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

(14) Murov, S. L.; Carmichael, I.; Hug, G. *L. Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(15) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; John Wiley & Sons: New York, 1986.

(16) Stretching vibration of carbonyl group of fluorenone, AF and 2DMAF measured by KBr method were 1715 cm^{-1} (fluorenone), 1680 cm^{-1} (1AF), 1713 cm^{-1} (2AF), 1686 cm^{-1} (3AF), 1707 cm^{-1} (4AF), and 1707 cm^{-1} (2DMAF), respectively. Other MAFs and DMAFs are shown in Experimental Section.

(17) (a) Boykin, D. W.; Nowak-Wyda, B. *Magn. Reson.* **1991**, *29*, 152. (b) Baumstark, A. L.; Graham, S. S.; Boykin, D. W. *Tetrahedron Lett.* **1990**, *31*, 957.

(18) ^{1}H NMR chemical shift (ppm) of amino proton in DMSO-d_6 at 30 °C were 6.68 (1AF), 5.62 (2AF), 6.45 (3AF), and 5.69 (4AF), respectively.

(19) Inoue, H.; Hoshi, T.; Yoshino, J.; Tanizaki, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1018; **1973**, *46*, 380. Tachibana, H.; Yatsuhashi, T.; Shimada, T.; Inoue, H., manuscript in preparation.

(20) Mataga, N.; Kaifu, Y.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 690. Lippert, E. *Z. Naturforsch.* **1955**, *10*, 541.

(21) In the absorption and fluorescence measurements for Lippert−Mataga plots, spectral grade solvent (Nacarai), diethyl ether, butyl acetate, ethyl acetate, THF, DMSO, DMF, acetone, and acetonitrile were used. In the estimation of dipole moment change by Lippert−Mataga equation, solute were assumed to have the spherical radius which has the same van der Waals volume of fluorenones. The radius and volume were 3.5 Å, 177 Å^3 (AF) and 3.7 Å, 212 Å^3 (3DMAF). The excited-state dipole moment of 4-aminofluorenone was estimated as 10.6−13 D by Hagan et al.: Hagan, T.; Pilloud, D.; Suppan, P. *Chem. Phys. Lett.* **1987**, *139*, 499.

(22) The solute radius and volume in the estimation were 3.6 Å, 194 Å^3 (2AAQ) and 3.8 Å, 237 Å^3 (2PAQ).

(23) The distance between the carbonyl oxygen and the hydrogen of amino group was calculated as 2.46 Å (1AF) and 1.84 Å (1AAQ) by MOPAC93 (PM3).

(24) Srivatsavoy, V. J. P.; Venkataraman, B.; Periasamy, N. *J. Photochem. Photobiol. A* **1992**, *68*, 169.

(25) Baumstark, A. L.; Dotrong, M.; Stark, R. R.; Boykin, D. W. *J. Chem. Soc., Chem. Commun.* **1989**, 767.

(26) Harju, T. O.; Huizer, A. H.; Varma, C. A. G. O. *Chem. Phys.* **1995**, *200*, 215.

(27) Fluorescence $\lambda_{\max}$ (nm) in ethanol at 77 K are 455 (shoulder), 490 and 512 (fluorenone); 502 (1AF); 530 (3AF); 555 (4AF); 506 (1MAF); 487 (shoulder) and 526 (3MAF); 564 and 597 (4MAF); 506 (1DMAF); 503 and 532 (3DMAF); 568 (4DMAF). 3-Substituted fluorenones showed weak vibronic structure, and the spectral shapes were very similar to that of fluorenone.

(28) Shirota, H.; Pal, H.; Tominaga, K.; Yoshihara, K. *J. Phys. Chem.* **1996**, *100*, 14575.

(29) Englman, R.; Jortner, J. *Mol. Phys.* **1970**, *18*, 145. Fread, K. F.; Jortner, J. *J. Chem. Phys.* **1970**, *52*, 6272.

(30) The ionization potentials of substituent were estimated as methane derivatives; methanol for −OH (10.85), methylamine for −NH$_2$ (8.97), dimethylamine for −NHCH$_3$ (8.24), trimethylamine for −N (CH$_3$)$_2$ (7.82), respectively. Hydroxy-9-fluorenones (HFs) were obtained from Nacarai (2HF, GR reagent), Aldrich (4HF, 98%). 1HF and 3HF were synthesized from the corresponding AFs by diazotization followed by hydrolysis and purified by recrystallization and served only for absorption measurement. Ionization potentials were referred from: Watanabe, K. *J. Chem. Phys.* **1957**, *26*, 542. Watanabe, K.; Mottl, J. R. *J. Chem. Phys.* **1957**, *26*, 1773.

(31) Yoshida, Z.; Takabayashi, F. *Tetrahedron* **1967**, *24*, 933.

(32) Matsuura, T. *Kagaku Ryouiki* **1969**, *23*, 858.

(33) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. R. *Chem. Phys. Lett.* **1973**, *19*, 315. Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971.

(34) Jones, G.; Feng, Z.; Bergmark, W. R. *J. Phys. Chem.* **1994**, *98*, 4511.

(35) Soujanya, T.; Fessenden, R. W.; Samanta, A. *J. Phys. Chem.* **1996**, *100*, 3507.

(36) Demeter, A.; Bérces, T.; Biczók, L.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Phys. Chem.* **1996**, *100*, 2001.