Effects of Molecular Structure and Hydrogen Bonding on the Radiationless Deactivation of Singlet Excited Fluorenone Derivatives[†]

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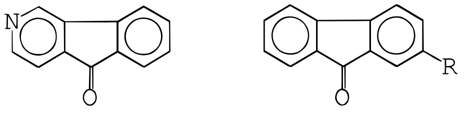
Substituent effects on intramolecular radiationless deactivation and hydrogen-bonding-induced quenching have been examined for various fluorenone derivatives. In toluene, triplet formation is the dominant process from the singlet excited state when an electron-withdrawing group is attached to the fluorenone moiety, whereas an electron-donating substituent promotes internal conversion. There is a clear correlation between the internal conversion rate constant and the lowest excited singlet state energy, which can be explained in terms of the energy gap law. It is shown that both the electron-donating character of the substituent in the excited fluorenone and the hydrogen-bonding power of alcohol play important roles in determining the rate of dynamic quenching by alcohols. The intermolecular hydrogen bonding with alcohols in the singlet excited state acts as an effective accepting mode of radiationless deactivation for fluorenones substituted with an electron-donating group. However, 2-NO_2− and 2-$COOCH_3$− derivatives are poorly quenched by alcohols. The parallel change of the hydrogen-bonding-induced quenching rate constants and the dipole moment difference between the ground and the singlet excited states suggests that the electron density around the carbonyl oxygen controls the quenching rate in the series of 2-substituted fluorenones.

Introduction

The effects of molecular structure, temperature, and microenvironment on the deactivation rate of excited molecules are among the most fundamental problems of photochemistry. Studies carried out in this field not only provide deeper insights into the microscopic mechanisms of relaxation processes and help to understand the fluorescence behavior of excited molecules but also contribute to the development and testing of theories regarding radiationless processes.[1−4]

Fluorenone is a particularly interesting molecule because its photophysical properties are extremely sensitive to the microenvironment.[5−10] We have shown that introduction of an electron-donating substituent alters the dominant energy dissipating pathways occurring from the singlet excited state.[11] The rate of the nonradiative decay of various aminofluorenone derivatives was found to vary considerably with molecular structure and solvent polarity.[12,13] It is well-known that hydrogen bonding often has a profound effect on fluorescent behavior, and various mechanisms are possible which explain the observed effects.[14] Singlet excited aromatic carbonyl compounds are quenched by alcohols[15−18] and hydroperoxides[18,19] via an excited hydrogen-bonded complex in which the hydrogen bond acts as an efficient accepting mode of radiationless deactivation. The hydrogen-bond strength sensitive solvatochromic properties of squaraine dyes can be exploited to probe the microenvironment in a variety of homogeneous and heterogeneous systems.[20]

The present paper focuses on the major factors governing the competition between internal conversion and triplet formation. In addition, we examine how the molecular structure of the excited molecule and the hydrogen-bonding power of the alcohol influence the rates of the hydrogen-bonding-induced energy dissipation processes. We used 2-substituted fluorenones in our studies because these species permitted systematic structural variations with consequent changes in such relevant parameters as excited-state energies, charge distribution, dipole moment, and hydrogen-bonding strength. A list of the investigated compounds is given in Figure 1.



−R	σ_p	−R	σ_p
−NO_2	0.78	−H	0.00
−$COOCH_3$	0.45	−OCH_3	−0.27
−$NHCOCF_3$	0.12	−NH_2	−0.66
−F	0.06	−$NHCH_3$	−0.70
		−$N(CH_3)_2$	−0.83

Figure 1. Formulas and list of compounds studied, with Hammett constants of the substituents (σ_p).

Experimental Section

Materials. Fluorenone and its 2-nitro, 2-carboxylic acid, 2-fluoro, 2-hydroxy, 2-amino, and 2-(dimethylamino) derivatives were obtained from Aldrich. 2-Methoxy-[21] and 2-$COOCH_3$-fluorenone[22] were synthesized as reported in the literature. 2-((Trifluoroacetyl)amino)fluorenone was prepared from 2-aminofluorenone with trifluoroacetic anhydride.[23] These fluorenone

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derivatives were purified by recrystallization and chromatography. 2,4,6-Trimethylpyridine (Aldrich) was distilled before use. The 3-azafluorenone[24] was kindly donated by Dr. Evan P. Kyba (Alcon Laboratories, Inc., Forth Worth, TX). The 2-(methylamino)fluorenone[12] was kindly provided by Dr. Tomoyuki Yatsuhashi (present address: Dept. of Chemistry, Osaka City University, Osaka, Japan). Alcohols (Aldrich) and the solvents (Merck, HPLC grade) were used as obtained. Samples were deoxygenated using freeze−pump−thaw cycles and then were sealed under vacuum.

Apparatus and Procedure. Corrected fluorescence spectra were recorded on a home-built spectrofluorometer equipped with a Princeton Applied Research type 1140 A/B photon-counting system. Fluorescence quantum yields were determined relative to that of quinine sulfate in a 1 N H_2SO_4 solution, for which a reference yield of 0.546 was used.[25]

Fluorescence lifetimes were measured, at the wavelength corresponding to the fluorescence maximum, using an Applied Photophysics SP-3 time-correlated single-photon-counting apparatus with a hydrogen lamp operated at 30 kHz. Data were analyzed by a nonlinear least-squares reconvolution method.

Triplet yields were determined from XeCl excimer laser flash photolysis experiments using the energy transfer method described in our previous paper.[11] However, perylene was employed as a triplet energy acceptor instead of 9,10-dibromoanthracene. The use of perylene offers several advantages: (i) Since its triplet yield is very low ($\Phi_{\rm Isc} = 0.014$),[26] only a very small correction is necessary for the triplet perylene formation via direct excitation. (ii) By virtue of its lower triplet energy ($E_{\rm T} = 148$ kJ mol^{-1})[27] perylene is a better energy acceptor than 9,10-dibromoanthracene. (iii) Its long triplet lifetime (5 ms)[27] facilitates more precise determination of the triplet−triplet absorbance after complete energy transfer. In these experiments the triplet perylene was detected at 490 nm and fluorenone in toluene was chosen as a reference because it has a well-established triplet yield ($\Phi_{\rm ISC} = 0.93$).[5,28]

The triplet yield of 2-CF_3CONH-fluorenone in acetonitrile determined by this technique showed good agreement with the results of another method where a fluorenone derivative served as an energy acceptor. In this method, we compared the triplet−triplet absorbances of the investigated compound in a sample where direct excitation was used with that where benzophenone triplet sensitizer was applied ($\Phi_{\rm ISC} = 1.00$).[27] The excitation and monitoring wavelengths were 351 nm (XeF laser) and 465 nm, respectively. Basically the same technique was applied for the determination of the 2-aminofluorenone triplet yield; however, in this case phenanthrene was the triplet sensitizer ($\Phi_{\rm T} = 0.73$),[29] and the signal was detected at 356 nm.

Equilibrium constants for the formation of 1:1 hydrogen-bonded complexes of ground-state fluorenone derivatives and alcohols were determined from the red-shift in the absorption spectrum caused by the added alcohol, as described in a previous publication.

Results and Discussion

Absorption and Emission Spectra. The absorption spectra of fluorenone and its 2-substituted derivatives in toluene are presented in Figure 2. The long-wavelength band shows a considerable red shift with decreasing electron-withdrawing and increasing electron-donating ability of the substituents. In addition, the separation of the first and second absorption bands becomes more pronounced in this series. The compound containing the strongest electron-withdrawing nitro group exhibits the smallest energy gap between these two bands. The spectral characteristics of 3-azafluorenone[30] were found to be similar to that of fluorenone. In the order from toluene to more polar solvents the position of the first absorption band hardly changes for 2-nitrofluorenone, while it always shows a bathochromic shift for the other compounds. The extent of the shift increases as the electron-donating ability of the substituent becomes stronger. These observations suggest that in toluene the lowest excited singlet state of 2-nitrofluorenone has some nπ* character, while the S_1 states of the other fluorenone derivatives are $\pi\pi$* states whose charge transfer character is enhanced as the electron-donating capability of the substituent increases.[12]

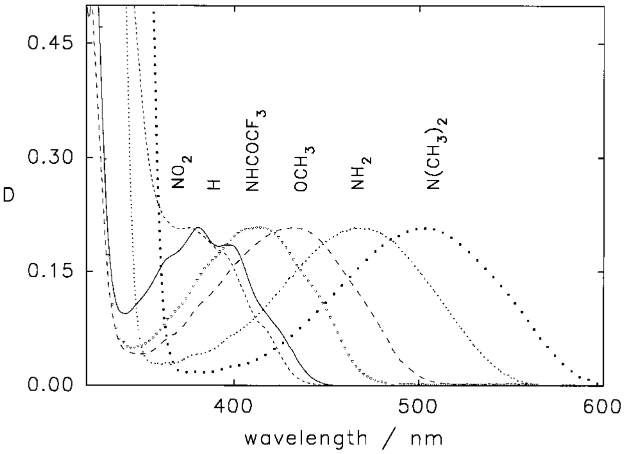

Figure 2. Absorption spectra of fluorenone derivatives in toluene.

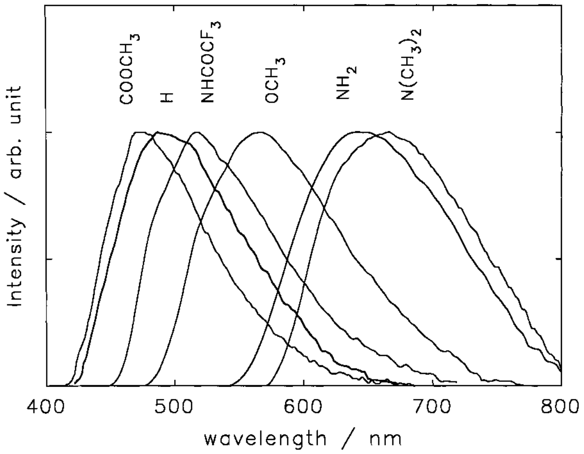

Figure 3. Fluorescence spectra of fluorenone derivatives in toluene.

Representative fluorescence spectra for 2-substituted fluorenones are shown in Figure 3. The fluorescence spectra appear to be mirror symmetrical with the long-wavelength band of the absorption spectra. The S_1 energies obtained from the location of the intersection of the normalized absorption and fluorescence spectra are given in the second column of Table 1. These results indicate a continuous decrease in the lowest excited singlet-state energy ($E(S_1)$) with increasing electron-donating ability of the substituent. Introducing an electron-withdrawing moiety into the fluorenone nucleus raises the energy of the S_1 state only slightly. For 2-nitrofluorenone, the S1 energy is estimated from the absorption spectrum because it does not fluoresce either in solutions at ambient temperature or in glass at 77 K.

In contrast to the other 2-substituted derivatives, where no phosphorescence can be identified ($\Phi_{\rm P} < 10^{-3}$), 2-nitrofluorenone emits intense phosphorescence at 77 K in organic glasses. Figure 4 shows the excitation spectra and the well-structured phosphorescence spectra both in ethanol and in methyltetrahy-

TABLE 1: Photophysical Properties of Fluorenone Derivatives in Toluene

R	$E(S1)$ (kJ mol^{-1})	Φ_{ISC}	$^1\tau$ (ns)	Φ_F	k_{ISC}	k_{IC} (s^{-1})	k_F
$-NO_2$	281	1.00	<0.5	0	>200		0
$-COOCH_3$	279	0.98	0.7	4.3	140	2.2	0.61
$-H$[a]	275	0.93	2.4	9.7	39	2.5	0.40
3-azafluorenone	268	0.93	1.9	8.2	49	3.2	0.43
$-F$[a]	266	0.72	10.8	22	6.7	2.4	0.20
$-NHCOCF_3$	260	0.38	9.0	27	4.2	6.6	0.30
$-OCH_3$[a]	245	0.16	4.0	9.2	3.1	19	0.23
$-NH_2$	221	0.02	0.8	1.0	2.5	120	0.13
$-NHCH_3$	212	<0.02	0.63[b]	1.0	<3.2	160	0.16
$-N(CH_3)_2$	206	<0.02	0.79[b]	1.1	<2.5	130	0.14

[a] Reference 11. [b] Reference 12, measured in benzene.

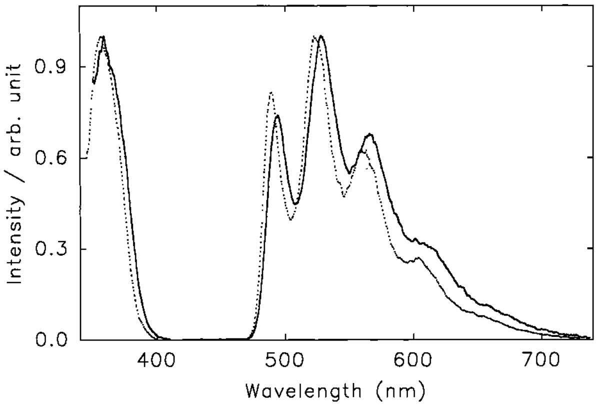

Figure 4. Phosphorescence spectra of 2-nitrofluorenone at 77 K in ethanol (···) and 2-methyltetrahydrofuran (—).

drofuran. Sharp vibrational progressions with $\Delta\nu \approx 1270$ cm^{-1} are seen in both organic glasses. Liptay et al. found a similar $\Delta\nu$ value (1200 cm^{-1}) in the absorption and fluorescence anisotropy spectra of unsubstituted fluorenone and attributed it to a C=O stretching vibration.[31] The blue shift of the excitation and phosphorescence spectra in ethanol as compared to that recorded in methyltetrahydrofuran (Figure 4) suggests that both the lowest singlet and triplet excited states of 2-nitrofluorenone are nπ^* type. The phosphorescence decay can be fairly well fitted by assuming first-order kinetics with a lifetime of about 0.015 s. The short triplet lifetime is in agreement with our assignment of the T_1 state to nπ^* type. It is well established that for the nπ^* triplet state the phosphorescence generally exhibits a prominent vibrational progression and its lifetime is typically in the millisecond range. To substantiate the assignment of the character of the T_1 state further, we performed laser flash photolysis studies. The triplet−triplet absorption spectrum of 2-nitrofluorenone was found to differ from that of other derivatives. The insert of Figure 6 shows that the triplet−triplet absorption maximum is located at 480 nm (red-shifted by 45 nm relative to that of fluorenone[8]). The well-separated weak band observed for fluorenone in the 550−700 nm range[8] appears as a tail of the strongest visible band in the case of the 2-nitro derivative. In addition, triplet 2-nitrofluorenone undergoes a hydrogen abstraction reaction with alcohols forming long-lived ketyl radicals, whereas the other triplet fluorenones are not quenched by alcohols. These observations also corroborate the evidence that, among the fluorenone derivatives studied, only 2-nitrofluorenone has an nπ^* lowest triplet state.

From the 0−0 transition of the phosphorescence spectra given in Figure 4, the $T_1(n\pi^*)$ energy is calculated to be 20 200 cm^{-1} = 242 kJ mol^{-1} in methyltetrahydrofuran and 20 400 cm^{-1} = 244 kJ mol^{-1} in ethanol. Huggenberger et al.[32] reported a considerably lower energy (17 600 cm^{-1} = 211 kJ mol^{-1}) for the $T_1(\pi\pi^*)$ state of unsubstituted fluorenone. Thus, the substitution of the fluorenone moiety with an electron-withdrawing nitro group not only increases the energy of the S_1 state but also that of the T_1 state.

Photophysical Properties. In order to avoid the interference originating from solvent−solute interactions, we studied the effect of molecular structure variations on the deactivation pathways of excited fluorenones in a nonpolar medium. Some of the derivatives have a low solubility in alkanes and cycloalkanes;therefore, toluene was chosen as solvent for the systematic investigations. Fluorescence decay times, $^1\tau_0$, fluorescence quantum yields, Φ_F, and triplet yields, Φ_{ISC}, are summarized in Table 1. Fluorescence quantum yields and lifetimes show parallel changes; they go through a maximum as a function of the energy of the lowest singlet excited state. An entirely different trend appears for triplet yields: Φ_{ISC}'s diminish by about 2 orders of magnitude through the series of compounds. In order to get a deeper insight into the factors controlling the rate of energy dissipating pathways of singlet excited molecules, the rate constants for fluorescence emission (k_F), intersystem crossing (k_{ISC}), and internal conversion (k_{IC}) were derived using the following expressions:

$$k_F = \Phi_F/{}^1\tau_0 \quad (1)$$

$$k_{ISC} = \Phi_{ISC}/{}^1\tau_0 \quad (2)$$

$$k_{IC} = (1 - \Phi_{ISC} - \Phi_F)/{}^1\tau_0 \quad (3)$$

It is evident from the data displayed in the last three columns of Table 1 that internal conversion is the fastest process from the singlet excited state for fluorenones containing electron-donating groups, whereas transition to a triplet dominates for the other derivatives. It is interesting to note that introducing heterocyclic nitrogen into the fluorenone moiety in position 3 scarcely affects the deactivation rates.

The fluorescence rate constants are much lower as compared to those of the nonradiative processes. The gradual decrease of k_F as a function of the S_1 energy can be rationalized in terms of the Strickler−Berg equation[33]

$$k_F = 2.88 \times 10^{-9}\, n^2\, (\bar{\nu}^{-3})_{av}^{-1} \int \epsilon\, d(\ln \bar{\nu})$$

where n is the refractive index of the solvent, $(\bar{\nu})_{av}^{-3^{-1}}$ denotes an average over the fluorescence spectrum, and the integral extends over the first absorption band. This relationship predicts that the radiative rate constants increase approximately as the cube of the emission energy.

The interpretation of the substituent effect on the rates of the nonradiative processes (presented in Table 1) can be based on the results obtained in previous studies[9−11] of the photophysics of fluorenone. It was shown that the dominant photophysical process of fluorenone in toluene is intersystem crossing to the triplet state. This occurs from the lowest excited singlet state by two competitive processes: a thermally activated transition to the adjacent T_3 state and a temperature-independent transition to the low-lying T_1 and T_2 states.

We attribute the very efficient intersystem crossing in toluene observed for 2-nitro, 2-carboxymethyl, and 3-aza derivatives as well as for fluorenone (and to some extent also for 2-fluorofluorenone) to the $S_1 \rightarrow T_3$ transition, which makes triplet state formation the prevailing photophysical process of these compounds.

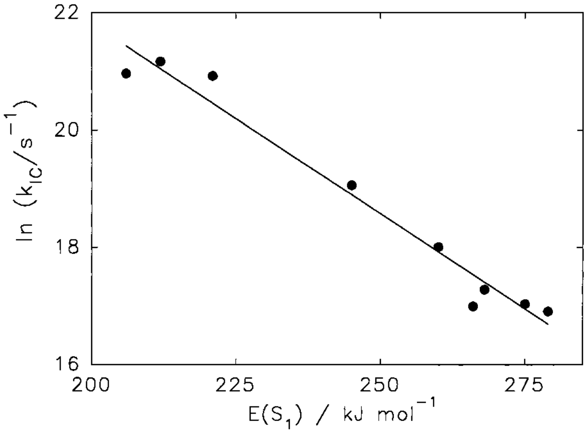

Figure 5. Logarithm of the internal conversion rate constant plotted as a function of the energy gap, Δ*E*, between the first excited singlet state and ground state.

However, replacement of the H-atom in position 2 by an electron-donating group decreases the S_1 state energy and thereby increases the S_1-T_3 energy gap. With such an increased energy gap, thermal activation is not able (at room temperature) to initiate the $S_1 \rightarrow T_3$ transition; consequently, triplet formation can occur only by $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ transitions. This explains the relatively low and constant intersystem crossing rates for the last five compounds in Table 1.

The rate of internal conversion also varies in the series of fluorenone derivatives; however, the tendency is opposite to that found for intersystem crossing. Internal conversion determines the photophysical behavior for fluorenone derivatives with electron-donating groups in position 2, but it plays a less important role for the other derivatives. Table 1 demonstrates a clear correlation between the internal conversion rate constant and the lowest excited singlet state energy, which can be expressed in quantitative form in terms of the energy gap law[34]

$$k_{IC} \propto \exp\,(-\gamma \Delta E / h\omega_M) \qquad (4)$$

where Δ*E* represents the energy gap between the excited and ground electronic states, $h\omega_M$ is the energy of the characteristic accepting mode, and *y* is considered a constant because it is a weakly varying function of Δ*E*. In Figure 5, ln k_{IC} is plotted as a function of the energy gap, Δ*E*. The good linear correlation indicates that the data satisfy eq 4 very well. Therefore, we conclude that the 2-substituted fluorenones share a common dominant accepting vibrational mode, and the underlying assumptions of the energy gap law are appropriate. On the basis of the k_{IC} vs Δ*E* relationship, the internal conversion rate of other 2-substituted fluorenone derivatives can be estimated from the singlet energy which is readily available from absorption or fluorescence spectra. Closely related studies on metal complexes,[35] carotenoids,[36] aromatic thiones,[37] and azulene derivatives[38] also demonstrated that the energy gap law is applicable for understanding and predicting the photophysical behavior of a variety of excited molecules.

Solvent Effect on the Rate of Deactivation Pathways. Triplet yields, fluorescence lifetimes, and fluorescence yields diminish going from toluene to more polar solvents for fluorenone derivatives substituted with an electron-donating moiety. As representative example, Table 2 summarizes the photophysical parameters of the 2-CF_3CONH derivative. The substantial increase in k_{IC} seen in acetonitrile can be rationalized in terms of the energy gap law. Interaction with the solvent decreases the energy of S_1 state and, consequently, accelerates the relaxation to ground state. An analogous phenomenon has been published for 2-methoxyfluorenone.[11] Since no triplet−triplet absorption can be detected for 2-NH_2-, 2-$NHCH_3$, and 2-$N(CH_3)_2$-fluorenone in polar solvents, we conclude that the lack of fluorescence in polar media can be attributed to the enhanced rate of internal conversion.

TABLE 2: Photophysical Behavior of 2-CF_3CONH-fluorenone in Various Solvents

solvent	Φ_{ISC}	$^1\tau$ (ns)	Φ_F	k_{ISC}	$10^{-7}\,k_{IC}$ (s^{-1})	k_F
toluene	0.38	9.0	0.027	4.2	6.6	0.30
ethyl acetate	0.12	9.9	0.025	1.2	8.6	0.25
CH_3CN	0.06	4.5	0.009	1.3	21	0.20

The solvent effect on the photophysical properties of 2-$COOCH_3$-fluorenone closely resembles that reported for fluorenone.[9] For example, the fluorescence lifetimes of 2-$COOCH_3$-fluorenone are 1.1, 2.6, 5.3, and 8.0 ns in ethyl acetate, acetone, dimethylformamide, and acetonitrile, respectively. The fluorescence yield shows a parallel increase with fluorescence lifetime; however, triplet yield decreases with increasing solvent polarity. The temperature dependence of k_{ISC} observed in hexane indicates that triplet formation can occur not only in the temperature-independent S_1-T_2 and S_1-T_1 processes but also via the endothermic S_1-T_3 transition. It has been demonstrated for fluorenone that the marked solvent effect originates from the change in S_1-T_3 energy difference. Due to interaction with the microenvironment, the S_1-T_3 energy gap increases with solvent polarity, and consequently, the rate of the thermal-enhanced intersystem crossing diminishes. Therefore, in polar media triplet formation can only take place via the slow, temperature-independent pathways.

In contrast with the analogous photophysical properties found in nonhydroxylic solvents, 2-$COOCH_3$-fluorenone and unsubstituted fluorenone exhibit remarkably different fluorescence behaviors in alcohols. The fluorescence lifetime of the 2-$COOCH_3$ derivative is much longer (4.6 ns in 1-octanol, 3.5 ns in ethanol) than that of fluorenone itself (1.2 ns in 1-octanol, 0.8 ns in ethanol).[10] This indicates that the rate of quenching caused by alcohols depends on the substituent. In order to clarify why the hydrogen-bonding interaction with the solvent induces only inefficient deactivation in the former case, we systematically studied the quenching kinetics of various fluorenone derivatives (vide infra).

The photophysical properties of 2-nitrofluorenone differ considerably from those found for the other fluorenone derivatives. Figure 6 shows the triplet−triplet absorption of 2-nitrofluorenone at 465 nm as a function of the laser intensity, for solutions that have matched optical densities at the laser wavelength (355 nm). It is apparent from the slopes that triplet yield does not change in various nonhydroxylic media ($\Phi_{ISC} = 1$) and decreases only slightly in ethanol ($\Phi_{ISC} = 0.91$). The high triplet yield may be explained by the fast intersystem crossing between close-lying $S_1(n\pi^*)$ and $T_3(\pi\pi^*)$ states. These transitions are favorable according to the El-Sayed rule.[39] The efficient triplet formation observed even in protic solvents such as ethanol suggests that the hydrogen-bonding-induced deactivation, which plays an important role for fluorenone,[16] cannot compete with the very fast intersystem crossing of singlet excited 2-nitrofluorenone ($k_{ISC} > 2 \times 10^9$ s^{-1}).

Interaction of Ground-State Fluorenone Derivatives with Aliphatic Alcohols. It was observed[16] that addition of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) to a solution of fluorenone in CH_2Cl_2 results in a considerable change in the absorption spectrum. Red shift and increased absorption were found in the 300−350 nm spectral region and were attributed to the formation

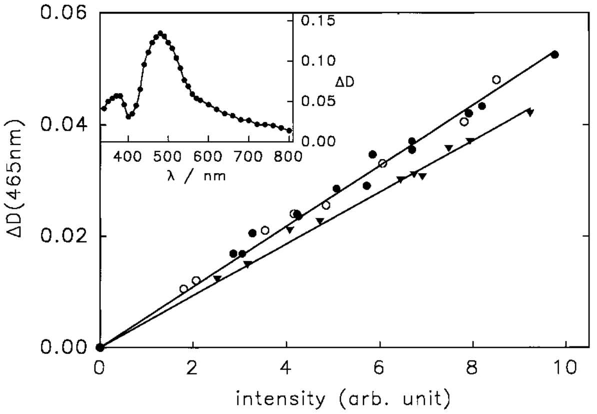

Figure 6. Initial triplet−triplet absorption of 2-nitrofluorenone at 465 nm vs laser intensity in toluene (●), in acetonitrile (○) and ethanol (▼). Insert: differential absorption spectrum of triplet 2-nitrofluorenone in toluene.

TABLE 3: Equilibrium Constants of Hydrogen Bonding between 2-Substituted Fluorenones and $(CF_3)_2CHOH$ in CH_2Cl_2

	−R				
	$-NO_2$	−H	−F	$-NHCOCF_3$	$-OCH_3$
K (dm^3 mol^{-1})	1.5	3.5[a]	2.2	2.1	2.4

[a] Reference 16.

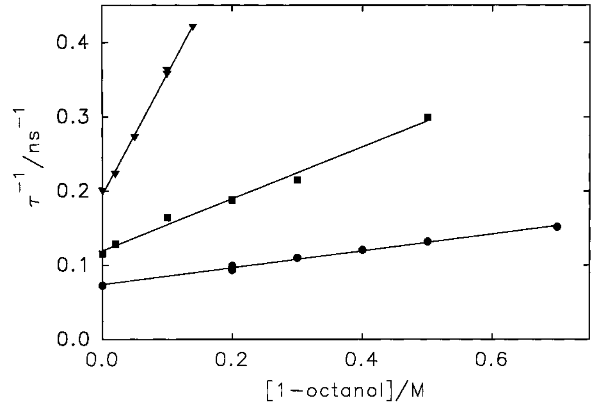

Figure 7. Reciprocal fluorescence lifetimes in CH_2Cl_2 vs 1-octanol concentration for fluorenone (●), its 2-CF_3CONH (▼) and 2-fluoro derivative (■).

TABLE 4: Dipole Moment Change upon Light Absorption and Rate Constants of Fluorescence Quenching by Alcohols for Fluorenone Derivatives

			10^{-9} k_q (M^{-1} s^{-1}) for quencher				
R−	$\Delta\mu$ (D)	solvent	$(CF_3)_2$-CHOH	CF_3-CH_2OH	CH_3-OH	CH_3-OD	1-octanol
CH_3O-	5.4	hexane	9.7	11	11	9.7	8.1
CF_3CONH-	5.5	hexane	15	17	12	11	6.4
CF_3CONH-	5.5	CH_2Cl_2	5.3	6.3	3.0	1.6	1.6
F−	3.9	CH_2Cl_2	7.8	7.1	0.87	0.38	0.37
H−[a]	3.5	CH_2Cl_2	4.6	3.2	0.21	0.16	0.11
3-azafluorene	3.2	CH_2Cl_2	6.0	2.8	0.11	0.05	0.055
CH_3OOC-	3.0	CH_2Cl_2	3.7	0.62	*b*	*b*	*b*

[a] Reference 16. [b] No dynamic quenching was observed.

of a 1:1 ground-state complex due to hydrogen bonding between fluorenone and the alcohol. We found similar spectral changes with 2-substituted fluorenones when alcohols were added and determined the equilibrium constants of hydrogen bonding from the shift of the absorption spectra. The equilibrium constants for hydrogen bonding of HFIP with fluorenone derivatives (Table 3) are rather low, and other aliphatic alcohols form even weaker hydrogen bonds.

Quenching of Singlet-Excited Fluorenone Derivatives with Aliphatic Alcohols. In order to clarify why the change from nonhydroxylic to alcohol solvents influences the photophysical properties of various fluorenone derivatives so differently, we examined the dependence of the hydrogen-bonding-induced deactivation kinetics on the molecular structure.

Addition of alcohol to the solutions of fluorenone derivatives shortens the lifetime of the lowest singlet excited state. The fluorescence decay, both in the absence and presence of alcohol, is well described by a single exponential function. This observation, along with the low hydrogen-bonding equilibrium constants in the ground state (see Table 3), indicates that dynamic quenching occurs. The significant increase in the negative charge density of the carbonyl oxygen upon light absorption promotes hydrogen-bonded complex formation in the singlet excited state.[12,18] A plot of the quenching of three fluorenone derivatives by 1-octanol in CH_2Cl_2 is shown in Figure 7. It can be seen that the reciprocal lifetimes increase linearly with alcohol concentration, and the rate constants derived from the slopes are markedly different for the various derivatives. In all cases, the quenching rate constants obtained from the fluorescence decay measurements are in good agreement with those derived from the Stern-Volmer plots of fluorescence and triplet yields. These results prove that the quenching of the singlet excited fluorenone and its derivatives by alcohols occurs via internal conversion rather than by some other photophysical process. Table 4 lists the change in dipole moments ($\Delta\mu$) of fluorenones upon excitation to S_1 states as well as the rate constants for the quenching of various fluorenone derivatives by alcohols (k_q). The $\Delta\mu$ values were derived from the solvent dependence of the fluorescence Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) using the Lippert−Mataga relationship:

$$\bar{\nu}_a - \bar{\nu}_f = \frac{2(\Delta\mu)^2}{cha^3}\left[\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 - 1}\right]$$

Here ϵ and n denote the dielectric constant and refraction index of the solvents, respectively. The spherical radius, a, was estimated to be 3.7×10^{-10} m for CH_3OOC- and CF_3CONH- derivatives, 3.3×10^{-10} for 3-azafluorenone and fluorenone, 3.4×10^{-10} and 3.5×10^{-10} m for F- and CH_3O-substituted fluorenones, respectively. The data given in Table 4 demonstrate that $\Delta\mu$ becomes smaller as the electron-donating ability of the substituent decreases in the series, and parallel change can be seen between the hydrogen-bonding-induced quenching rate constants (k_q) and the dipole moment differences in the ground and the singlet excited states, $\Delta\mu$.

In hexane, fluorenones substituted with strongly electron donating CH_3O- or CF_3CONH- groups react with alcohols at rates which are close to the diffusion-controlled limit. Because an increase in solvent polarity is known to decrease the strength of hydrogen bonding,[40] the lower k_q, obtained when changing the solvent from hexane to CH_2Cl_2, is in accordance with the suggestion that hydrogen bonding enhances nonradiative deactivation.

The involvement of hydrogen bonding between a singlet excited fluorenone derivative and alcohol in the quenching process is further demonstrated by the dependence of the quenching rate constant on the structure of alcohol. A decreasing tendency is observed in the k_q values when the quencher is changed from fluorinated alcohols through methanol to 1-octanol (Table 4). This sequence corresponds to the decreasing hydrogen-bonding ability of the alcohols, as measured by the hydrogen-bonding equilibrium constant[41] determined for the alcohols with a common acceptor (*N*-methylpyrrolidinone) in 1,1,1-trichloroethane solvent. The significant deuterium isotope effect found for quenching by CH_3OH/D indicates that hydrogen bonding in the excited state provides an efficient accepting mode for radiationless deactivation to the ground state. The k_H/k_D ratio ranges from 1.3 to 2.2 when the rate is well below the diffusion-controlled limit.

It is especially noteworthy that in methylene chloride the rate of quenching by alcohols decreases monotonically as the dipole moment of the singlet excited state becomes smaller. It is evident from the data presented in Table 4 that this tendency is valid for the reactions of all five alcohols. Throughout the series of fluorenone derivatives the smallest k_q change (less than a factor of two) is seen for HFIP which has a high hydrogen-bonding power. Using weakly hydrogen-bonding alcohols (e.g. methanol and 1-octanol) the decrease in k_q is so large that no dynamic quenching can be detected for the fluorenone derivative containing the electron-withdrawing $-COOCH_3$ group. The parallel change between the dipole moment of the singlet excited state and the quenching rate constant can be rationalized by considering the variation in the hydrogen-bonding strength within the incipient substituted fluorenone−alcohol excited complexes (exciplexes). As pointed out above, substitution of fluorenone alters the charge distribution predominantly in the excited state. Thus, the hydrogen-bonding ability of fluorenones is more sensitive to variations in the molecular structure while in the excited state than in the ground state. Introducing an electron-donating group into the fluorenone skeleton increases the negative charge density on the carbonyl oxygen and thereby increases the hydrogen-bond-accepting power of the singlet excited molecule. Electron-withdrawing substituents have the opposite effect. They reduce the electron density on the carbonyl oxygen and, as a result, decrease the strength of the hydrogen bonding with alcohols. Since the vibronic mode associated with hydrogen bonding in the excited state favors a radiationless transition to the ground state, the weakening of the hydrogen bond results in lower quenching rates.

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References and Notes

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