

Substituent and solvent effects on the photophysical properties of 3-azafluorenone derivatives

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Abstract

Fluorescence lifetimes, fluorescence yields and triplet yields have been determined for 3-azafluorenone and its 7-substituted derivatives in various solvents. The energy of the lowest excited singlet state and the rate of intersystem crossing are found to be significantly higher in hexane relative to those in more polar solvents. The substitution with fluor and methyl groups as well as the solvent polarity enhancement considerably decelerate the triplet formation. This effect is attributed to the increase in the activation energy of the transition from the lowest singlet to a close-lying higher triplet excited state. The internal conversion gains in importance with increasing solvent polarity and becomes the major excited state depopulating process for the substituted derivatives in polar media. The changes in the internal conversion rate constants can be rationalized based on the energy gap law. © 2001 Published by Elsevier Science B.V.

Keywords: Fluorescence; Triplet yield; Intersystem crossing; Internal conversion

1. Introduction

The photophysical properties of fluorenone derivatives have recently attracted considerable attention, because they are excellent model compounds for the study of the effect of molecular structure [1–5], temperature [6,7] and microenvironment [8–12], on the rate of the radiationless deactivation. Systematic investigations have elucidated the major factors determining the competition among the various relaxation processes and revealed the mechanism of the hydrogen bonding induced quenching [1,13–16]. In spite of the widespread current interest in the excited fluorenones, the fluorescent behavior and the energy dissipation processes of their nitrogen heterocyclic homologues have not been studied yet.

Azafluorenones are important in several respects. They serve as precursors to the synthesis of physiologically active compounds. Their hydantoins and succinimide derivatives have been shown to be aldose reductase inhibitors [17,18]. An important class of natural alkaloids, the onychine derivatives, possesses azafluorenone moiety [19]. Moreover, 1,8-diazafluorenone is an outstanding reagent for the detection of α -amino acids by fluorescence method. It is substantially more sensitive than ninhydrin and particularly

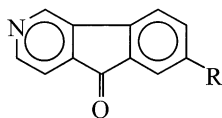
advantageous for automated amino acid analysis as well as in forensic science [20].

The main goal of the present paper is to elucidate how the introduction of heterocyclic nitrogen in the position three of the fluorenone moiety alters the fluorescent behavior and the kinetics of the transitions undergoing from the singlet excited state. In addition, we reveal how the solvent polarity and the substitution influence the dominant excited state deactivation pathway and the rate of the various relaxation processes. The results are compared with those for fluorenones to gain more insight into the effect of molecular structure on the photophysical properties. A list of the investigated compounds is given in Scheme 1.

2. Experimental details

The 3-azafluorenone derivatives were kindly provided by Dr. Evan P. Kyba (Alcon Laboratories Inc., Forth Worth, TX, USA). The synthesis of the compounds has already been described [21]. HPLC grade solvents (Merck) were used as obtained. Samples were deoxygenated by purging with nitrogen of high purity. Corrected fluorescence spectra were recorded on a home-built spectrofluorimeter equipped with a Princeton Applied Research type 1140 A/B photon-counting system. Fluorescence quantum yields were determined relative to that of fluorenone in acetonitrile for which a reference yield of $\Phi_F = 0.032$ was taken [6,7]. Fluorescence

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Scheme 1. Investigated compounds: R = H, F, CH₃.

lifetimes were measured 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 non-linear least-squares deconvolution method. Intersystem crossing quantum yields were determined from XeCl excimer laser flash photolysis experiments using the energy transfer method described in our previous paper [1].

3. Results

3.1. Absorption and fluorescence spectra

Fig. 1 shows the absorption spectra of 3-azafluorenones in hexane and acetonitrile. In the latter solvent no vibrational structure appears and the bands are red-shifted relative to those in hexane. Introduction of the fluor and the methyl substituent in the position 7 of the 3-azafluorenone moiety leads to slight bathochromic shift of the long-wavelength band. The position of the second band changes only for the fluor derivative where small blue shift can be observed.

The fluorescence spectra are mirror symmetrical with the long-wavelength band of the absorption spectra. The solvent and the substituent effects on the fluorescence spectra resem-

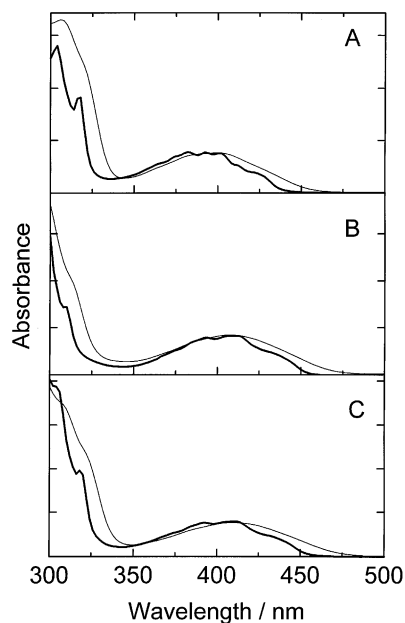


Fig. 1. Absorption spectra of 3-azafluorenone (A); 7-fluor-3-azafluorenone (B); and 7-methyl-3-azafluorenone (C) in hexane (heavy line) and acetonitrile (thin line).

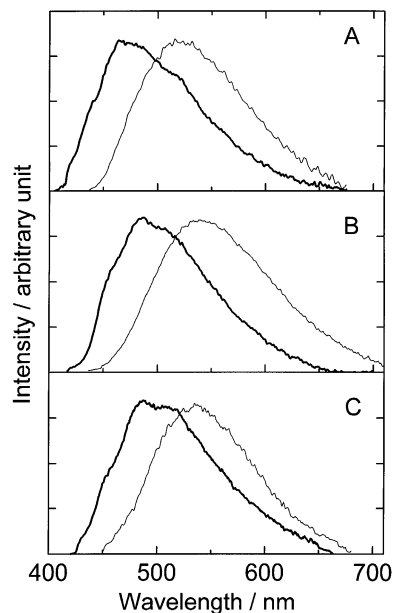


Fig. 2. Fluorescence spectra of 3-azafluorenone (A); 7-fluor-3-azafluorenone (B); and 7-methyl-3-azafluorenone (C) in hexane (heavy line) and acetonitrile (thin line).

ble to the corresponding changes in the first absorption band. Representative fluorescence spectra are presented in Fig. 2. The energies of the lowest singlet excited state ($E(S_1)$) were derived from the location of the intersection of the normalized absorption and fluorescence spectra. The results, summarized in Table 1, clearly demonstrate the decrease of $E(S_1)$ with increasing $E_T(30)$ solvent polarity parameter. It is especially noteworthy that the $E(S_1)$ of all 3-azafluorenones is considerably higher in hexane than the other media. Despite the similar polarity of hexane and toluene, the excited state energy diminishes more going from the former to the latter media than throughout the series of the other solvents indicating that the character of the lowest singlet excited state is different in hexane.

3.2. Photophysical parameters

The photophysical properties exhibit a peculiar solvent dependence. The most remarkable features of the results presented in Table 1 are the short fluorescence lifetime (τ_F) and low fluorescence yield (Φ_F) of all 3-azafluorenones in hexane. As the triplet yield is close to unity, intersystem crossing is the dominant deactivation pathway from the singlet excited state in this solvent independently of the substituent.

Changing the solvent from toluene to acetonitrile results in dissimilar tendency in the fluorescent behavior for 3-azafluorenone and its 7-substituted derivatives. In the latter case, the Φ_F and τ_F values go through a maximum whereas for the former compounds, monotonous increase is seen as the function of solvent polarity. The triplet yields of azafluorenones show parallel change in the series of sol-

Table 1
Photophysical parameters of 3-azafluorenone derivatives in various solvents at 295 K

Solvent	$E_T(30)$ (kJ mol ⁻¹)	$E(S_1)$ (kJ mol ⁻¹)	Φ_{ISC}	τ_F (ns)	Φ_F (10 ⁻³)	k_{ISC} (10 ⁷ s ⁻¹)	k_{IC} (10 ⁷ s ⁻¹)	k_F (10 ⁷ s ⁻¹)
3-Azafluorenone								
Hexane	129	279	0.97	<0.6	0.4	>160	^b	>0.06
Toluene	142	269	0.92	2.2	8.6	42	3.2	0.39
Etac ^a	160	267	0.86	2.4	9.4	35	5.4	0.39
CH ₂ Cl ₂	170	266	0.56	6.1	22	9.2	6.9	0.36
CH ₃ CN	191	264	0.53	6.7	24	7.9	6.7	0.36
7-Fluoro-3-azafluorenone								
Hexane	129	269	0.96	<0.6	1.7	>160	^b	>0.28
Toluene	142	262	0.65	4.5	12	14	7.5	0.27
Etac	160	259	0.49	6.6	20	7.4	7.4	0.30
CH ₂ Cl ₂	170	259	0.25	6.3	18	4.0	12	0.29
CH ₃ CN	191	257	0.14	5.6	15	2.5	15	0.27
7-Methyl-3-azafluorenone								
Hexane	129	268	0.88	<0.7	3.2	>125	^b	>0.46
Toluene	142	259	0.65	6.6	31	9.8	4.8	0.47
Etac	160	258	0.47	7.4	36	6.4	6.7	0.48
CH ₂ Cl ₂	170	255	0.19	5.9	22	3.2	13	0.37
CH ₃ CN	191	254	0.15	5.3	19	2.8	16	0.36

^a Ethyl acetate.

^b Too small compared with k_{ISC} .

vents but the extent of diminution is much larger for the substituted derivatives, where internal conversion becomes the major excited state depopulating process in polar media.

3.3. Rate constants of excited state deactivation

In order to reveal how the environment and the molecular structure affects the competition between the various energy dissipation channels, the rate constants for fluorescence emission (k_F), intersystem crossing (k_{ISC}) and internal conversion (k_{IC}) were derived using the expressions given below:

$$k_F = \frac{\Phi_F}{\tau_F} \quad (1)$$

$$k_{ISC} = \frac{\Phi_{ISC}}{\tau_F} \quad (2)$$

$$k_{IC} = \frac{1 - \Phi_{ISC} - \Phi_F}{\tau_F} \quad (3)$$

The results displayed in Table 1 demonstrate that the solvent influences the photophysical processes mainly by controlling the rate of intersystem crossing. Although only lower limit can be given for k_{ISC} in hexane because of the weak fluorescence and the limited time resolution of our instrument, it is clearly seen that particularly rapid triplet formation takes place in this apolar solvent. The k_{ISC} markedly decreases with increasing polarity of the media. Opposite trend, rate constant enhancement, appears for the internal conversion going from toluene to acetonitrile. In polar solvents radiationless relaxation to the ground state becomes the dominant process depopulating the singlet excited state

of the substituted derivatives. The radiative rate constants proved to be insensitive to the molecular structure and solvent variation.

4. Discussion

The experimental data demonstrate that the introduction of the heterocyclic nitrogen atom in the position 3 of the fluorenone moiety leads only to minor changes in the photophysical properties. For the related compounds, azabenzophenones, conflicting reports can be found in the literature regarding how the position of the nitrogen in the aromatic ring affects the excited state behavior. Theoretical calculations suggested that the charge distribution of the 4-aza derivative resembles the most to that of benzophenone [22,23]. In contrast, the spectroscopic characteristics, triplet yields and lifetimes of 3-aza isomer were found to be the most similar to those of benzophenone [24]. Our results, in agreement with the latter studies, show that the introduction of heterocyclic nitrogen in the three position exerts relatively small effect because of the limited possibility for conjugation with the carbonyl group. Since the absorption and fluorescence spectra as well as the photophysical properties of the 3-azafluorenone closely resemble to those of fluorenone, the $n\pi^*$ states associated with the heterocyclic nitrogen atom seems to be located at higher energies and therefore, are not involved in the photophysical processes in liquid phase. Hence, the interpretation of the results summarized in Table 1 can be based on the knowledge obtained in previous studies of fluorenone and its derivatives [6,7,25,26].

The fluorescence yield and lifetime of 3-azafluorenone was found to be temperature dependent. For example, the fluorescence lifetimes in ethyl acetate are 2.2 and 4.1 ns at 296 and 242 K, respectively, whereas the fluorescence quantum yield increases from 0.0094 to 0.017 in this temperature range. These facts indicate that intersystem crossing from the singlet excited state takes place not only via the usual transition to lower-lying triplet levels but also in thermal enhanced process to a triplet state (T_n) whose energy is only slightly higher than that of the S_1 state. In apolar solvents, where S_1 and T_n are adjacent, the $S_1 \rightarrow T_n$ transition is accelerated by its low activation energy and consequently, rapid triplet formation takes place. On the other hand, increasing solvent polarity decreases the energy of S_1 state and thereby, expands the S_1-T_n energy gap. The continuous slowing down of triplet formation in the series of solvents (Table 1) arises mainly from the enhanced activation energy of the $S_1 \rightarrow T_n$ process. However, the remarkably high k_{ISC} in hexane indicates that the coupling between singlet and triplet excited states is more efficient in this solvent compared to more polar media. Similar effect was reported for fluorenone and 2-fluoro-fluorenone and it was shown that not only the low activation energy but also the large Arrhenius pre-exponential factor of the thermal enhanced intersystem crossing leads to the more rapid triplet formation in aliphatic hydrocarbons [6,7].

It is interesting to note that in acetonitrile k_{ISC} is significantly higher for 3-azafluorenone compared to that of fluorenone ($2.5 \times 10^7 \text{ s}^{-1}$) [6]. Due to the large S_1-T_n energy gap, thermally activated triplet formation cannot occur in the case of the latter compound in polar media [6]. In contrast, 3-azafluorenone possesses temperature dependent k_{ISC} even in such a polar solvent as acetonitrile (the $\tau_F = 6.7$ ns fluorescence lifetime at 295 K grows to 9.6 ns at 242 K and a simultaneous decrease of triplet yield can be observed). The T_n level is located closer to the S_1 state for the 3-aza derivative, hence the thermal energy around room temperature is enough to bring about the $S_1 \rightarrow T_n$ process which contributes to the rate of temperature independent transitions to lower-lying triplet states. The substituent effect on k_{ISC} apparent from Table 1 is explained also by the change of the S_1-T_n energy gap. Introduction of the fluor and particularly the electron donating methyl groups makes the $S_1 \rightarrow T_n$ transition more endothermic and thereby, decelerates the triplet formation.

The rate of internal conversion also varies in the series of solvents for all 3-azafluorenones, however, the tendency is opposite to that found for intersystem crossing. Table 1 demonstrates a clear correlation between the internal conversion rate constant and the lowest excited singlet state energy. As it is expected based on the energy gap law [27,28], interaction with solvents diminishes the singlet excited state energy and the vibrational coupling enhancement caused thereby leads to substantial increase in k_{IC} . Lower k_{IC} is found for 3-azafluorenone in all solvents compared

with the corresponding values for the substituted derivatives. This fact is the consequence of the higher excited state energy of the former compound. Because of the higher excited state dipole moment, solvent-solute interaction stabilizes the S_1 state of the substituted derivatives to a larger extent, which promotes more rapid relaxation to the ground state.

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