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Laser flash photolysis study of the photochemistry of 4,5-diaza-9-fluorenone

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The triplet excited state of 4,5-diaza-9-fluorenone (**1**) shows absorption maxima at 410 and 470 nm and a lifetime of 3 μs, in acetonitrile. Its intersystem crossing quantum yield was determined using 9-fluorenone as a secondary standard and a value of 0.41 ± 0.01 was obtained. The reactivity of the triplet excited state of **1** towards several quenchers, in acetonitrile, was investigated employing the laser flash photolysis technique quenching rate constants ranging from $7.9 \times 10^4\,M^{-1}\,s^{-1}$ (2-propanol) to $1.0 \times 10^{10}\,M^{-1}\,s^{-1}$ (triethylamine) were obtained. From the quenching rate constants obtained one can conclude that 4,5-diaza-9-fluorenone has a $\pi\pi^*$ triplet excited state. A Hammett plot for the quenching rate constants of triplet **1** by phenols containing polar substituents against σ^+ gave a reaction constant ρ of -1.54 ± 0.10, which demonstrates the electrophilic character of the 4,5-diaza-9-fluorenone triplet excited state.

1. Introduction

The photochemical reactivity of the triplet excited state of aromatic ketones is one of the most studied processes in organic photochemistry not only in organic solvents but also in organized media [1–7]. There is an appreciable difference in reactivity between $n\pi^*$ and $\pi\pi^*$ states for a given triplet carbonyl. One of more dramatic examples of this difference in reactivity is shown by xanthone. The n,π^* triplet excited state of xanthone is highly reactive in non-polar media, such as alkanes. On the other hand, in polar solvents the lowest energy triplet excited state has π,π^* character, and shows little tendency of hydrogen abstraction [8,9]. The introduction of a nitrogen atom in the aromatic ring of xanthone leads to 1-azaxanthone, which has been proved to be efficiently photoreduced in both polar and non-polar media [10–12].

In the case of benzophenone, the replacement of a phenyl by a pyridyl group leads to an enhancement of its reactivity toward hydrogen abstraction reactions, with the photophysics and photochemistry of dipyridyl ketones depending on the position of the nitrogen atom in the aromatic ring as well as on the solvent polarity, with both effects cooperating in the determination of their excited state properties [6,13–16].

Recent work from our group showed that the laser flash photolysis of 1,4-diaza-9-fluorenone and 1,4-diaza-benz[b]-9-fluorenone in acetonitrile leads to formation of the corresponding triplets, which have absorption maxima in the 400–500 nm region and lifetimes in the order of few microseconds, with energies around 50 kcal/mol. The triplet excited state of both 1,4-diazafluorenones was effectively quenched by electron donors such as DABCO ($k_q \approx 10^9\,M^{-1}\,s^{-1}$). However, for quenchers in which the primary process corresponds to hydrogen transfer, such as 2-propanol or 1,4-cyclohexadiene, quenching rate constants of around $10^5\,M^{-1}\,s^{-1}$ were measured. This behavior indicates that the photochemistry of 1,4-diaza-9-fluorenone and 1,4-diaza-benz[b]-9-fluorenone is dominated by a triplet excited state of $\pi\pi^*$ character [17] .

The present work is aimed to study the reactivity of the triplet excited state of 4,5-diaza-9-fluorenone, in acetonitrile, toward several quenchers that can behave as pure hydrogen donors, such as 1,4-cyclohexadiene, 2-propanol, toluene or cyclohexane, as hydrogen donors through a proton-coupled electron transfer, such as indole or phenol and its derivatives containing polar substituents on the aromatic ring and, finally, toward electron donors,

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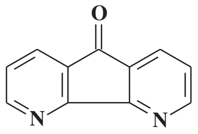
such as 1,4- diazabicyclo[2.2.2]octane (DABCO) and triethylamine. Triplet energy acceptors such as 1,3- cyclohexadiene, β-carotene, *E*- and *Z*-stilbenes were also used.



2. Materials and methods

2.1. Reagents

The solvents acetonitrile, benzene and methanol, all spectroscopic grade, were purchased from Aldrich. 4,5-diaza-9-fluorenone (**1**) was purchased from Aldrich and recrystallized from methanol/water. The quenchers *E*- stilbene, *Z*-stilbene, toluene, β-carotene, 2-propanol, cyclohexane, triethylamine, 1,4-diazabicyclo[2.2.2]octane (DABCO), indole, phenol, 4-aminophenol, 4-hydroxyphenol, 4- methoxyphenol, 4-fluorphenol, 4-cyanophenol, 4-*tert*-butylphenol, 4-bromophenol, 4- chlorophenol, 4-phenylphenol, 3-chlorophenol, 4-methylphenol, 3-methylphenol, 3-methoxyphenol were purchased from Aldrich and used as received. 1,3-Cyclohexadiene and 1,4-cyclohexadiene (from Aldrich) were bulb-to-bulb distilled just prior to use.

2.2. Instruments

UV–visible spectra were obtained on a Varian Cary 3E spectrophotometer. The laser flash photolysis experiments were conducted on a Luzchem instrument, model mLFP 122. In all experiments 10 mm × 10 mm Suprasil cells containing 3.0 mL solution of the corresponding fluorenone in acetonitrile were used, with the solutions being deaerated with oxygen- free nitrogen for 20 min. The samples were irradiated with the 3rd harmonic ($\lambda = 355$ nm, ~5 ns, 40 mJ/pulse) of a Nd/YAG Surelite laser controlled by a Dell computer, 4700 series, which uses a Labview 4.1 (National Instruments) application. The concentration of fluorenone was chosen to obtain an absorbance of ~0.3 at the excitation wavelength (355 nm). Stock solutions were prepared in the same solvent used for sample preparation, so that it was only necessary to add microliter volumes to the cell to obtain the appropriate quencher concentrations.

2.3. Intersystem crossing quantum yield

In the laser flash photolysis technique the concentration of triplets formed after the pulse can be determined at low concentrations of sample and low laser power. In this case the initial concentration of triplets (ΔA_o) measured at zero time after the laser pulse has a linear dependence on the excitation energy (*E*). Thus, the intersystem crossing quantum yield for a given sample can be determined from the slope of a plot of *E* versus ΔA_o which is then compared to a standard (9-fluorenone in acetonitrile, $\Phi_{isc} = 0.48$), assuming that the difference between the molar absorptivity for the ground state and the excited triplet state ($\varepsilon_G - \varepsilon_T$) remain constant. For this measurement, solutions of unknown and standard must have exactly the same absorbance at the excitation wavelength and the molar absorptivity for the triplet excited state of both the unknown ($\varepsilon_T^{1,4\text{-diaza-9-fluorenone}}$) and the standard ($\varepsilon_T^{9\text{-fluorenone}}$) must be known. However, since in this case the pair standard/unknown shows great similarity between their orbitals, one can accept as a reasonable approximation that $\varepsilon_T^{9\text{-fluorenone}} = \varepsilon_T^{4,5\text{-diaza-9- fluorenone}}$ [18].

The intersystem crossing quantum yield for 4,5-diaza-9-fluorenone was calculated employing 9-fluorenone in acetonitrile as a secondary standard, for which a value of 0.48 can be found in the literature [16,18]. Thus, matched samples (absorbance at 308 of 0.225) of 9-fluorenone and 4,5-diaza-9-fluorenone were excited with a Lumonics Excimer laser TE-860-2 ($\lambda = 308$ nm, ~5 ns, ≥80 mJ/pulse) and the laser energy was attenuated by the use of neutral density filters with transmittance values of *T* = 10, 40, 50, 63.1, 79.4 and 100%. From the slope of the plots of ΔA at time zero after the laser pulse versus %*T* and employing the Eq. (1), the φ_{isc} for 4,5 -diaza-9-fluorenone was obtained [18].

$$\frac{\text{slope for } 4,5 - \text{diaza} - 9 - \text{fluorenone}}{\text{slope for } 9 - \text{fluorenone}} = \frac{\phi_{ces}4,5\text{−diaza} - 9 - \text{fluorenone}}{\phi_{ces}9\text{−fluorenone}} \quad (1)$$

3. Results and discussion

Laser flash photolysis ($\lambda_{exc} = 355$ nm) of a solution of 4,5-diaza-9-fluorenone in acetonitrile led to the formation of a transient with absorption maxima at 410 and 470 and a shoulder at 560 nm (Fig. 1), whereas in benzene these maxima are located at 490 and 510 nm (Fig. 1S, Supporting information). In methanol, a wide band with maximum at 430 nm and a shoulder at 570 nm (Fig. 2S, Supporting information) could be observed. In acetonitrile, this transient followed either at 410 or at 470 nm has a lifetime of 3 μs and its decay shows a first-order kinetics with a strong 2nd-order contribution (Fig. 1, inset), which is usually associated with a deactivation process involving triplet-triplet annihilation [19]. It is worth noting that 4,5-diaza-9fluorenone does not show any phosphorescence either at room temperature or at 77 K.

The intersystem crossing quantum yield (φ_{isc}) for 4,5-diaza-9-fluorenone in acetonitrile was calculated using Eq. (1) and employing 9-fluorenone as the secondary standard ($\varphi_{isc} = 0.48 \pm 0.03$), in this same solvent [16–18]. From the slope of the plots of ΔA at time zero after the laser pulse versus %*T* (Fig. 3S, Supporting information) and employing the Eq. (1) a value of 0.41 ± 0.01 for the φ_{isc} of 4,5- diaza-9-fluorenone was obtained. This value is slightly lower when compared to that for 9-fluorenone and can be

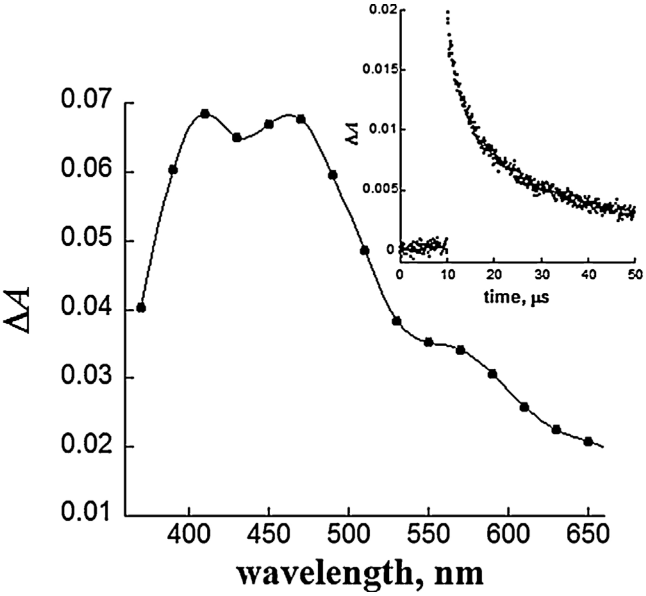


Fig. 1. Absorption spectrum for the transient generated upon the excitation ($\lambda = 355$ nm) of 4,5-diaza-9-fluorenone in acetonitrile and recorded 1.8 μs after the laser pulse. Inset: decay for this transient monitored at 470 nm.