ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 94 (1996) 7–13

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

Substituent effects on carbocation photophysics: 9-arylxanthyl and 9-arylthioxanthyl carbocations

Joanne M. Bedlek, Maria R. Valentino, Mary K. Boyd

Department of Chemistry, Loyola University of Chicago, Chicago, IL 60626, USA

Received 22 March 1995; accepted 26 July 1995

Abstract

Substituent effects on the photophysical properties of 9-arylxanthyl and 9-arylthioxanthyl cations have been examined. These properties include fluorescence quantum yields, excited-state lifetimes, radiative and non-radiative rate constants. A dramatic substituent effect is observed on these properties for the xanthyl cations, with an increase in the electron-donating ability of the substituents resulting in a decrease in the fluorescence lifetimes and quantum yields and a corresponding increase in the non-radiative rate constants. In contrast, little or no substituent effect is seen in the thioxanthyl cation series. Possible explanations for the differing substituent effects are considered.

Keywords: Carbocations; Photophysics; Fluorescence; Substituent effects; Xanthylium ions; Thioxanthylium ions

1. Introduction

There has been considerable recent interest in the photochemistry of carbocations, particularly mechanistic and reactivity studies [1], complementing early photoproduct studies [2]. In the photoproduct studies, the cations were generated thermally in strongly acidic media, with subsequent irradiation. The isolated photoproducts resulted from photoisomerization, intramolecular rearrangements or photoinduced electron transfer [3–7]. Recent laser flash photolysis studies provided direct evidence for electron transfer reactions of carbocations [8–10]. Both singlet and triplet excited xanthyl and thioxanthyl cations undergo electron transfer processes with aromatic compounds generating the corresponding xanthyl radical and the radical cation of the aromatic donor. In addition to direct detection of the radical and radical cation, further evidence for electron transfer processes came from correlation of the quenching rate constants with the ionization potential of the aromatic donor, as well as the isolation of radical-derived photoproducts [11].

The fluorescence from singlet excited xanthyl cations is quenched by water, alcohols and ethers, proposed to act as nucleophilic quenchers [12–15]. The quenching rate constants are several orders of magnitude larger than the corresponding ground-state values, indicating an enhanced electrophilicity in the excited state [12]. Substituent effects on the fluorescence quenching from 9-arylxanthyl cations show that the bimolecular quenching rate constants increase as the substituent becomes more strongly electron donating. Hammett plots of of $\log[k_q(X)/k_q(H)]$ vs. $\sigma^{h\nu}$ [16] gave negative ρ values for each quencher [13–15]. In contrast, ground-state xanthyl cations reacting with nucleophilic species exhibit the opposite substituent effect [17]. Application of the Rehm–Weller equation [18] with $E_{1/2}{}^{\text{red}}$ values for the 9-arylxanthyl cations eliminated electron transfer as a possible mechanism for quenching by water, alcohols and ethers [15]. Shukla and Wan ruled out electron transfer as the mechanism for quenching of singlet excited thioxanthyl cations by water, owing to the absence of radical coupling products and the inability to trap any putative radicals [19].

Attention has also focused on the characterization of excited-state carbocations. Both singlet and triplet carbocations have been characterized by fluorescence, phosphorescence and laser flash photolysis methods [8–10,12–14,19–22]. The numerous cations studied include the xanthyl, thioxanthyl, dibenzosuberenyl and triphenylmethyl cations. We have reported a substantial substituent effect on the fluorescence lifetimes of various 9-arylxanthyl carbocations [13,14]. There are other limited reports of aryl substituent effects on fluorescence lifetimes and quantum yields for these cations [9]. However, there has been no systematic study of substituent effects on carbocation photophysics. This is in contrast to a recent report of substituent effects on carbanion photophysics in which both the identity and the location of the substituent in several 9-arylfluorenyl anions affected the excited-state lifetime [23]. Specifically, anions substituted

1010-6030/96/$15.00
SSDI 1010-6030(95)04187-7

with *meta*-withdrawing or *para*-donating groups produced the shortest lifetimes. These substituent effects on the fluorescence lifetimes were rationalized by differences in the S_0–S_1 energy gap.

Herein we report a photophysical study of several 9-arylxanthyl and 9-arylthioxanthyl cations. Significant differences in substituent effects on the fluorescence quantum yields, lifetimes and photophysical parameters are observed between the xanthyl and thioxanthyl systems. Possible explanations accounting for these differences are considered.

2. Experimental details

2.1. Instrumentation

Melting points were taken on a Mel-Temp melting point apparatus and are uncorrected. UV and visible absorption spectra were measured on a Hewlett Packard 8452A diode array spectrophotometer. Fluorescence measurements were obtained on a Photon Technology International LS-100 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Varian VXR300 instrument operating at 300 Hz for ^{1}H and 75 Hz for ^{13}C. ^{1}H NMR signals are reported in parts per million (δ) from tetramethylsilane as an internal standard. ^{13}C NMR chemical shifts were reported with reference to the 77.0 ppm NMR peak for $CDCl_3$.

2.2. Materials

All ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solvent obtained from Aldrich Chemical Company. Anhydrous tetrahydrofuran used in Grignard syntheses was dried over calcium hydride and then freshly distilled. Arylbromides were obtained from Aldrich and distilled prior to use. Spectroscopic grade acetonitrile used in UV, steady state and fluorescence lifetime measurements was obtained from Mallinckrodt. Residual water was removed by passing the acetonitrile through a column of neutral aluminum oxide obtained from Aldrich. Propionic anhydride and fluoroboric acid used in the syntheses of thioxanthylium tetrafluoroborate salts were obtained from Aldrich and used as received.

2.3. Fluorescence measurements

Fluorescence quantum yields of both the 9-arylxanthyl and the 9-arylthioxanthyl cations in dry acetonitrile were measured vs. quinine sulfate monohydrate in 0.1 N H_2SO_4 using $\Phi_f = 0.52$ [24]. Fluorescence lifetimes of **1a**–**1e** and **2a**–**2d** were measured in dry acetonitrile using a nanosecond flash lamp filled with nitrogen. Excitation of the cations was at 381 nm (N_2) and emission monitored at 540 nm for the xanthyl cations and 573 nm for the thioxanthyl cations with a 350 nm cut-off filter placed before the emission monochromator to eliminate excitation and Raman scattering. All measured lifetimes were independent of cation concentration below 5.0×10^{-5} M. The fluorescence lifetime of **1f** was estimated from relative fluorescence intensities [14]. Steady state fluorescence emission was measured using a pulsed Xe lamp apparatus and the 350 nm cut-off filter previously described.

2.4. Syntheses

2.4.1. 9-Arylxanthylium tetrafluoroborate salts

Xanthylium salts **1a**–**1f** were prepared according to a literature procedure [14]. Their spectral data (^{1}H and ^{13}C NMR, absorption and fluorescence spectra) were consistent with those previously reported [14].

2.4.2. 9-Arylthioxanthen-9-ols

Alcohols **3a**–**3d** were prepared by Grignard reaction of the appropriate arylmagnesium bromide (8.7 mmol) and recrystallized thioxanthone (4.40 mmol) in anhydrous tetrahydrofuran. The reaction mixture was heated at reflux temperature for 1 h. Aqueous workup followed by purification with silica gel chromatography using methylene chloride as eluant and subsequent recrystallization from 95% ethanol gave the pure 9-arylthioxanthenols as white solids.

9-Phenylthioxanthen-9-ol (**3a**): yield, 0.50 g (39%); melting point, 103–107 °C (literature melting point, 106 °C [25]); ^{1}H NMR, $\delta = 2.76$ (s, 1H), 7.00–8.05 (m, 13H); UV at 216 nm ($\epsilon = 29\,700$), 268 nm ($\epsilon = 11\,000$).

9-(4'-Fluorophenyl)thioxanthen-9-ol (**3b**): yield, 23 mg (17%); melting point, 140–142 °C (literature melting point, 141–142 °C [26]); ^{1}H NMR, $\delta = 2.79$ (s, 1H), 6.86–8.08 (m, 12H); UV at 216 nm ($\epsilon = 30\,000$), 266 nm ($\epsilon = 13\,000$).

9-(3'-Fluorophenyl)thioxanthen-9-ol (**3c**): yield, 53 mg (2.2%); melting point, 123–125 °C; ^{1}H NMR, $\delta = 2.78$ (s, 1H), 6.74–8.02 (m, 12H); ^{13}C NMR, $\delta = 164.09$, 160.83, 146.21, 146.12, 139.29, 131.29, 129.49, 129.38, 127.55, 127.29, 126.60, 126.40, 126.11, 122.49, 114.78, 114.48, 114.20, 113.90, 73.37; UV at 216 nm ($\epsilon = 28\,200$), 266 nm ($\epsilon = 12\,000$).

9-(4'-Methylphenyl)thioxanthen-9-ol (**3d**): yield, 46 mg (7%); melting point, 161–163 °C (literature melting point, 164–165 °C [27]); ^{1}H NMR, $\delta = 2.29$ (s, 3H), 2.81 (s, 1H), 6.88–8.11 (m, 12H); UV at 216 nm ($\epsilon = 26\,600$), 266 nm ($\epsilon = 9400$).

2.4.3. 9-Arylthioxanthylium tetrafluoroborate salts

Thioxanthyl salts **2a**–**2d** were prepared following the method of Dauben et al. [28]. The corresponding 9-arylthioxanthen-9-ol (0.1 mmol) was dissolved in propionic anhydride (0.27 ml) at room temperature or slightly higher, where heat was provided by a warm water bath. This temperature was maintained on the addition of fluoroboric acid (19 mg, 0.22 mmol), which immediately gave a red solution. The thioxanthylium tetrafluoroborate salt precipitated and was collected by suction filtration. The salts were washed repeatedly with cold, anhydrous diethyl ether to yield a bright red solid in every case.

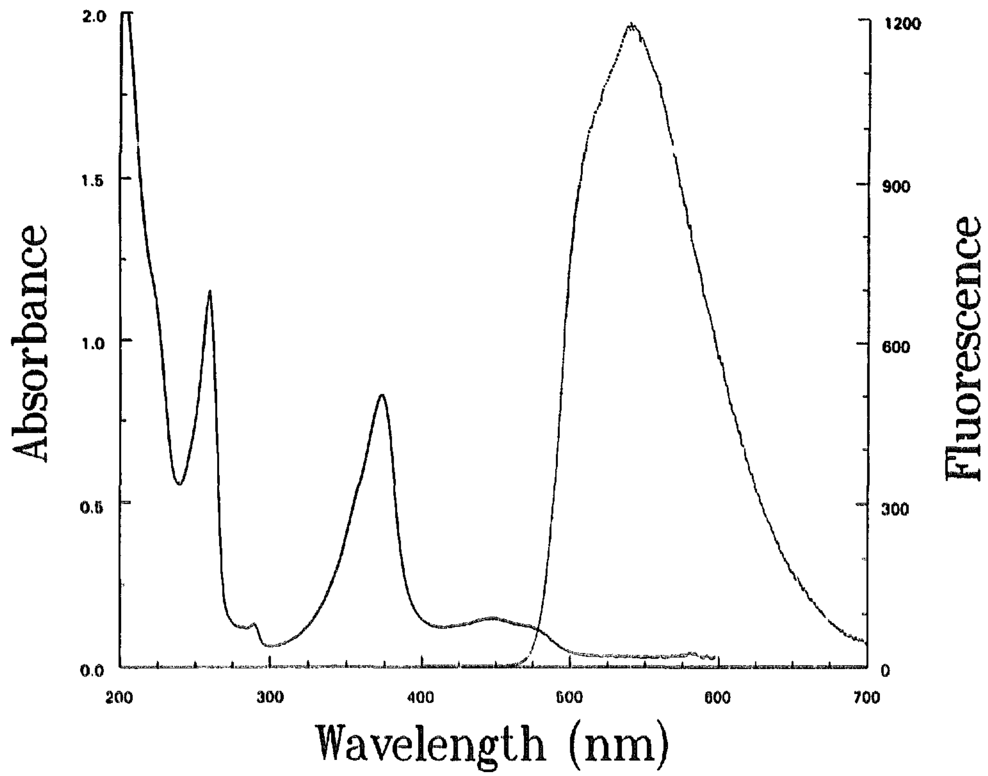


Fig. 1. Absorption spectrum (——) and fluorescence spectrum (·····) for the 9-phenylxanthyl tetrafluoroborate salt **1a** in acetonitrile. The fluorescence intensity is in arbitrary units.

9-Phenylthioxanthylium tetrafluoroborate (**2a**): yield, 10 mg (27%); melting point, 194–196 °C, decomposes; ^{1}H NMR, δ=7.00–8.88 (m, 13H); ^{13}C NMR, δ=170.72, 146.60, 137.56, 135.40, 134.40, 131.13, 130.98, 130.21, 129.56, 129.07, 128.23; UV at 218 nm (ϵ=22 500), 246 nm (ϵ=14 000), 278 nm (ϵ=39 700), 384 nm (ϵ=17 400), and 494 nm (ϵ=5600).

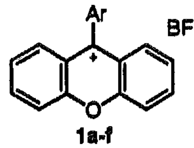
9-(4'-Fluorophenyl)thioxanthylium tetrafluoroborate (**2b**): yield, 48 mg (49%); melting point, 218–220 °C, decomposes; ^{1}H NMR, δ=6.88–9.09 (m, 12H); ^{13}C NMR, δ=141.72, 138.72, 138.53, 133.08, 132.3, 132.15, 130.02, 129.91, 128.16, 127.39, 127.35, 127.25, 116.95, 115.16, 114.88; UV at 220 nm (ϵ=22 400), 246 nm (ϵ=12 400), 278 nm (ϵ=38 900), 384 nm (ϵ=18 100), and 496 nm (ϵ=4800).

9-(3'-Fluorophenyl)thioxanthylium tetrafluoroborate (**2c**): yield, 9.9 mg (17%); melting point 208–210 °C, decomposes; ^{1}H NMR, δ=7.28–8.88 (m, 12H); ^{13}C NMR, δ=164.07, 160.74, 148.79, 137.37, 136.17, 136.07, 134.87, 131.16, 131.03, 130.92, 129.97, 128.20, 126.63, 125.54, 125.49, 118.10, 117.82, 117.04, 116.72; UV at 220 nm (ϵ=18 500), 246 nm (ϵ=10 000), 280 nm (ϵ=40 200), 386 nm (ϵ=12 400), and 494 nm (ϵ=3800).

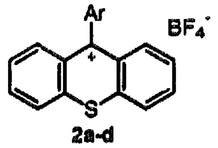
9-(4'-Methylphenyl)thioxanthylium tetrafluoroborate (**2d**): yield, 11 mg (49%); melting point, 134–136 °C, decomposes; ^{1}H NMR, δ=2.63 (s, 3H), 7.30–8.86 (m, 12H); ^{13}C NMR, δ=141.72, 138.72, 138.53, 133.08, 132.30, 132.15, 130.02, 129.91, 128.16, 127.39, 127.35, 127.25, 116.95, 115.16, 114.88; UV at 218 nm (ϵ=25 400), 246 nm (ϵ=11 800), 282 nm (ϵ=38 900), 382 nm (ϵ=11 800), and 496 nm (ϵ=5200).

3. Results

We chose for our substrates the 9-arylxanthyl tetrafluoroborate salts **1a–1f** and the 9-arylthioxanthyl tetrafluoroborate salts **2a–2d**.



1a-f



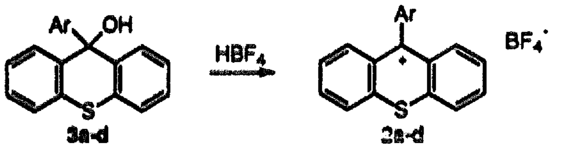
2a-d

Aryl substituent: **a**=H, **b**=*p*-F, **c**=*m*-F, **d**=*p*-CH$_3$, **e**=*m*-CH$_3$, **f**=*m*-OCH$_3$

We have previously reported the synthetic procedure for preparation of cation salts **1a–1f** and their spectroscopic characterization [14]. Absorption maxima at 260, 374 and 450 nm are observed for each of **1a–1f** in acetonitrile. These absorption spectra are identical to those obtained for the same cations prepared from their corresponding alcohols in acidic organic [8–12] or aqueous [13,20] solvents. Excitation at 370 nm of **1a–1f** in acetonitrile solution gives a broad fluorescence emission band centered at 530 nm, with a mirror image relationship to the ground-state cation absorption spectra. Fig. 1 illustrates absorption and emission spectra for **1a**.

These spectra are representative of those obtained for each of **1a–1f**, as no substituent effect is observed on the wavelengths of either the absorption or the emission spectra.

The 9-arylthioxanthyl tetrafluoroborate salts **2a–2d** were prepared using the same synthetic procedure developed for the xanthyl salts [14]. Initially, the 9-arylthioxanthen-9-ols **3a–3d** were synthesized by Grignard reaction of the appropriate arylmagnesium bromide with thioxanthone. Treatment of alcohols **3a–3d** with fluoroboric acid in propionic anhydride gave the thioxanthyl salts as stable, red crystalline solids.



Absorption spectra of **2a–2d** in acetonitrile exhibited maxima at 280, 384 and 494 nm. Excitation at 382 nm gave a broad unstructured emission band centered at 575 nm. As with the 9-arylxanthyl cations, no substituent effect is observed on the position of the absorption or emission spectra, with representative spectra shown in Fig. 2 for **2a**. The absorption and emission spectra of **2a** and **2b** are identical to those previously reported for the same cations generated from their corresponding alcohols in aqueous acidic solution [19] or acidified acetonitrile [8,9].

Fluorescence lifetimes were measured for **1a–1f** in acetonitrile (Table 1). The lifetimes of **1a**, **1b**, **1d** and **1e** are in very good to excellent agreement with literature values [8–10,12,13]. The lifetimes display a dramatic substituent dependence, with the lifetimes varying from 28 ns for the parent cation **1a** to a subnanosecond value for the *m*-OMe substituted cation **1f**. Fluorescence lifetimes for the thioxanthyl cations **2a–2d** exhibit very different behavior. In contrast to the large substituent effect on lifetimes for the xanthyl cations, there is apparently no substituent effect on the 9-arylthioxanthyl cations. Each of **2a–2d** exhibits a single-exponential lifetime of approximately 1 ns (Table 1). A fluorescence lifetime of 1 ns has been previously reported

Table 1
Photophysical data for 9-arylxanthyl and 9-arylthioxanthyl cations

Compound	τ_F [a] (ns)	Φ_F [b]	k_{dt} (s^{-1})	k_f [c] (s^{-1})	k_{nr} (s^{-1})
1a	27.6	0.47 ± 0.01	3.6×10^7	1.7×10^7	1.9×10^7
1b	18.8	0.28 ± 0.02	5.3×10^7	1.5×10^7	3.8×10^7
1c	14.0	0.18 ± 0.01	7.1×10^7	1.3×10^7	5.8×10^7
1d	2.1	0.014 ± 0.001	4.8×10^8	6.7×10^6	4.7×10^8
1e	2.0	0.084 ± 0.001	5.0×10^8	4.2×10^7	4.6×10^8
1f	0.028	$(6.6 \pm 0.8) \times 10^{-4}$	3.6×10^9	2.4×10^7	3.6×10^9
2a	1.0	0.020 ± 0.001	1.0×10^9	2.0×10^7	9.8×10^8
2b	1.0	0.018 ± 0.001	1.0×10^9	1.8×10^7	9.8×10^8
2c	1.3		7.8×10^8		
2d	1.0	0.011 ± 0.001	1.0×10^9	1.1×10^7	9.9×10^8

[a] Fluorescence lifetimes for **1a–1f** were taken from Ref. [14].

[b] Errors quoted are the standard deviations obtained from repeated measurements.

[c] Calculated from $k_f = \Phi_F / \tau_F$.

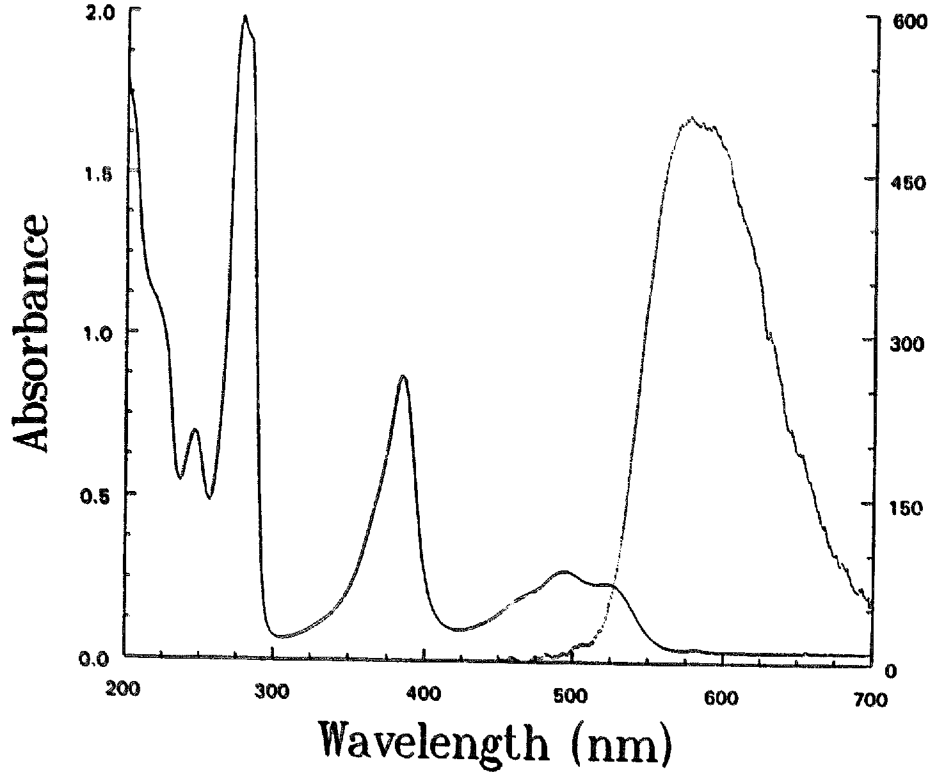


Fig. 2. Absorption spectrum (——) and fluorescence spectrum (·····) for the 9-phenylthioxanthyl tetrafluoroborate salt **2a** in acetonitrile. The fluorescence intensity is in arbitrary units.

[8] for the 9-phenylthioxanthyl cation generated from its corresponding alcohol in 1:1 acetonitrile–trifluoroacetic acid (ACN–TFA), in excellent agreement with the value reported here. Lifetime estimates of less than 2 ns for the parent and *p*-F substituted thioxanthyl cations [9] in trifluoroethanol–trifluoroacetic acid (TFA–TFE) are also in agreement with our values.

Fluorescence quantum yields were measured for **1a**–**1f** and **2a**–**2d** in acetonitrile (Table 1) relative to quinine sulfate. Our quantum yield of 0.47 for the parent 9-phenylxanthyl cation **1a** is in excellent agreement with values of 0.48 (in 1:1 ACN–TFA), 0.42 (in acetonitrile with 8% H_2SO_4) and 0.45 (in 3 M TFA–ACN) reported by Das and colleagues [8,12]. However, it is in poorer agreement with reported values of 0.80 (in 1% TFA in TFE) and 0.33 (in 0.1 M TFA in TFE) [9,10]. Since the 9-phenylxanthyl cation is quenched by water with a rate constant of 2.02×10^7 M^{-1} s^{-1} [14], the lower quantum yield values may be explained by traces of water in the solvent. Similarly, our quantum yield of 0.28 for **1b** is somewhat lower than the reported value of 0.55 (also in 1% TFA in TFE) [9]. Again, it is possible that trace amounts of water may be responsible for the lower value reported here. Our fluorescence quantum yield of 0.020 for **2a** is in very good agreement with reported values of 0.025 (in 1:1 ACN–TFA [8]) and 0.031 (in TFA–TFE [9]). Similarly, our quantum yield of 0.018 for **2b** is in excellent agreement with a reported value of 0.020 (in TFA–TFE [9]).

Substituent effects on the fluorescence quantum yields for the xanthyl and thioxanthyl cations follow the pattern observed in the lifetime measurements, that is little or no effect on quantum yields for the thioxanthyl cations, with a large effect in the xanthyl cations. The quantum yields in the xanthyl series range from a high of 0.47 for the parent cation **1a** to a value of only 6.6×10^{-4} for the *m*-OCH_3 cation **1f**. The trend in the quantum yields for the 9-arylxanthyl cations parallels that seen for the lifetimes, namely a decrease in both the fluorescence lifetimes and the quantum yields as the substituents become more strongly electron donating. In contrast to the substituent effect in the xanthyl series, there is only a modest substituent effect on the fluorescence quantum yields for the thioxanthyl cations **2a**–**2d**. The quantum yields vary from 0.020 for **2a** to a low of 0.011 for **2d**.

Total decay rate constants k_{dt} were calculated from the lifetimes for **1a**–**1f** and **2a**–**2d** (Table 1) for comparison with those reported for resonance stabilized carbanions [23]. As indicated by the lifetimes, a dramatic substituent effect is observed in k_{dt} for the xanthyl cations, with decay rate constants ranging from 3.6×10^7 s^{-1} for **1a** to 3.6×10^9 s^{-1} for **1f**. Decay rate constants at the upper end of the range are associated with the more strongly electron-donating substituents. In contrast to the xanthyl cations, no substituent effect is seen on k_{dt} for the thioxanthyl cations, whose decay rate constants of approximately 1.0×10^9 s^{-1} are at the upper end of the range observed for the xanthyl cations.

Fluorescence and non-radiative rate constants k_f and k_{nr} respectively were calculated from the fluorescence quantum yields and lifetimes for **1a**–**1f** and **2a**–**2d** (Table 1). The fluorescence rate constant of 1.7×10^7 s^{-1} for **1a** is in excellent agreement with the value of 1.7×10^7 s^{-1} determined by Das and colleagues from fluorescence quantum yields and lifetime measurements [8]. Das and coworkers also calculated a k_f value of 2.5×10^7 s^{-1} for the 9-phenylxanthyl cation using the Strickler–Berg formula [29], which is in very good agreement with our fluorescence rate constant. A k_f value of 2.5×10^7 s^{-1} was determined from the fluorescence quantum yield and lifetime for the 9-phenylthioxanthyl cation and a value of 2.4×10^7 s^{-1} from the Strickler–Berg formula [8]. Our k_f value of 2.0×10^7 s^{-1} for **2a** is in very good agreement with these literature values.

Interestingly, the fluorescence rate constants display only a modest substituent effect in both the xanthyl and thioxanthyl series, ranging from a low of 6.7×10^6 s^{-1} for **1d** to a high of 4.2×10^7 s^{-1} for **1e**, and ranging between 2.0×10^7 s^{-1} for **2a** and 1.1×10^7 for **2d**. However, a large substituent effect is seen on the rate constants for non-radiative decay with the xanthyl cations, ranging from 1.9×10^7 s^{-1} for **1a** to 3.6×10^9 s^{-1} for **1f**. The largest values for k_{nr} are associated with the cations substituted with the more strongly electron-donating substituents. No substituent effect is observed for k_{nr} with the thioxanthyl cations, with a rate constant of 9.8×10^8 s^{-1} determined for each of **2a** and **2b**, and a k_{nr} value of 9.9×10^8 s^{-1} for **2d**.

4. Discussion

Substituent effects on the photophysical properties of the 9-arylxanthyl cations demonstrate that an increase in the electron-donating ability of the aryl substituent results in a decrease in the fluorescence lifetimes and quantum yields, with a corresponding increase in the non-radiative rate constants. Studies of the 9-arylfluorenyl anions show that both *meta*-withdrawing and *para*-donating groups give rise to higher k_{dt} values (shorter lifetimes) and lower fluorescence quantum yields [23]. These substituent effects on the fluorenyl anion photophysical properties were rationalized using the energy gap law [30]. The energy of lowest wavelength emission maximum was chosen as an estimate for $E_{0,0}$ because of the well-resolved vibronic structure in the emission spectra. A plot of $\ln(k_{nr})$ vs. ΔE gave very good correlation, providing a rationalization of the photophysical properties by intrinsic properties. This approach cannot be applied to the 9-arylxanthyl cations, as they exhibit no substituent effect on either the absorption or emission spectra. Each of the cations **1a**–**1f** give spectra which are virtually superimposable.

Another possibility which may account for the observed photophysical properties of the 9-arylxanthyl cations is a substituent effect on intersystem crossing of the singlet excited cations to the triplet state. The triplet states of both the 9-phenylxanthyl and the *p*-fluoro substituted cations were characterized by transient absorption spectroscopy and phosphorescence measurements [9]. The *p*-OMe substituted 9-arylxanthyl cation exhibits a short singlet lifetime and low fluorescence quantum yield; however, a high rate constant for intersystem crossing was ruled out as a possible explanation as no phosphorescence could be detected at room temperature for this cation. Instead, a rapid intramolecular charge transfer quenching was proposed as a possible deactivational mechanism. Indeed, the *p*-OMe substituted xanthyl cation exhibits an absorption spectrum different from each of the other 9-aryl xanthyl cations. Its absorption spectrum includes a long wavelength absorption band that is not well resolved and is shifted to 500 nm. Each of the 9-arylxanthyl cations **1a**–**1f** displays an absorption band at 450 nm (Fig. 1), ruling out intramolecular charge transfer as an explanation for the short lifetimes and quantum yields for the other 9-arylxanthyl cations substituted with strongly electron-donating groups.

A substituent effect on the rate constant for intersystem crossing may account for the substituent dependence on the fluorescence lifetimes and other photophysical parameters for **1a**–**1f**. However, it cannot account for the observed substituent effect on the quenching of the singlet excited 9-arylxanthyl cations by water, alcohols and ethers, in which electron-donating substituents increase the magnitude of the quenching rate constants [13–15]. Nevertheless, we measured phosphorescence spectra for the xanthyl cations to examine the possibility of a substituent effect on the phosphorescence quantum yields. 370 nm excitation of the xanthyl cation solutions at 77 K gave very weak phosphorescence spectra, at the extreme sensitivity level of our spectrometer. No differences in phosphorescence intensity could be detected. Previous reports of the phosphorescence spectra for some 9-arylxanthyl cations also noted very weak emission, without comment on the relative intensity for the different substituents [9]. The absence of a substituent effect on the phosphorescence quantum yields does not completely rule out the possibility of a substituent on intersystem crossing, since the triplet to singlet radiative rate constants are not necessarily identical for each of the substituted cations.

The 9-arylthioxanthyl cations exhibit little or no substituent effect on their photophysical properties. Each of **2a**–**2d** exhibits a fluorescence lifetime of 1.0 ns. One possible explanation which may account for the short lifetime and rapid non-radiative decay of the thioxanthyl cations is a second excited state that is close in energy to the fluorescent state. This condition is observed for the benzyl radical which is non-fluorescent at room temperature but has a fluorescence lifetime of 10–20 ns at low temperature [31]. To investigate this possibility with the thioxanthyl cations, we measured the fluorescence lifetime of **2a** at 77 K. Whereas the cation has a cleanly single-exponential fluorescence decay with a lifetime of 1.0 ns at room temperature, a second small component (about 10%) with a lifetime of 16 ns is observed at the lower temperature. This does suggest the possibility of a second electronic state that may be responsible for the rapid non-radiative decay, with a weak temperature dependence on the excited state lifetime for the thioxanthyl cations.

An alternate possibility that may account for the absence of a substituent effect on the thioxanthyl cations is the sulfur heteroatom causing an enhanced intersystem crossing to the triplet state, an influence which might overwhelm any effects due to the 9-aryl substituent. We examined the phosphorescence spectrum from the 9-phenylthioxanthyl cation, to compare its phosphorescence intensity with that of the 9-phenylxanthyl cation. As described for the 9-arylxanthyl cations, only very weak phosphorescence could be detected from **2a** in agreement with previous reports [9], with no observable increase in intensity compared with **1a**. Again, this does not definitely rule out an enhanced intersystem crossing in the thioxanthyl series, since the triplet to singlet radiative rate constants may differ between the xanthyl and thioxanthyl cations.

Another possibility that may account for the different photophysical behavior of the thioxanthyl cations is a structural change due to the presence of a sulfur heteroatom in the central xanthyl ring resulting in a greater twisting of the 9-aryl ring away from planarity, decreasing potential conjugative interactions from substituents on the 9-aryl ring. To investigate this possibility, we carried out geometry optimization calculations on the 9-phenylxanthyl and 9-phenylthioxanthyl cations at the AM1 level. The minimized structures show that the 9-phenyl ring is twisted 59° out of planarity (where a 90° twist represents the structure with the 9-phenyl ring perpendicular to the xanthyl backbone). In contrast, the 9-phenyl ring in the thioxanthyl case has a twist angle of 68°. Less conjugative interactions are suggested in the thioxanthyl system, in accord with our experimental results.

Acknowledgments

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. M.R.V. also thanks the Arthur J. Schmitt Foundation for a Dissertation Fellowship.

References

[1] P.K. Das, *Chem. Rev.*, *93* (1993) 119.

[2] R.F. Childs and G.B. Shaw, *Org. Photochem.*, *11* (1991) 111. R.F. Childs, *Rev. Chem. Intermed.*, *3* (1980) 285. P.W. Cabell-Whiting and H. Hogeveen, *Adv. Phys. Org. Chem.*, *10* (1973) 129.

[3] E.E. van Tamelen, T.M. Cole, R. Greeley and H. Schumacher, *J. Am. Chem. Soc.*, *90* (1968) 1372.

[4] E.E. van Tamelen and T.M. Cole, *J. Am. Chem. Soc.*, *93* (1971) 6158.

[5] E.D. Owen and D.M. Allen, *J. Chem. Soc., Perkin Trans. II*, (1973) 95.

[6] D.M. Allen and E.D. Owen, *J. Chem. Soc., Chem. Commun.*, (1971) 848.

[7] D. Bethell and P. Clare, *J. Chem. Soc., Perkin Trans. II*, (1972) 1464.

[8] A. Samanta, K.R. Gopidas and P.K. Das, *J. Phys. Chem.*, *97* (1993) 1583. A. Samanta, K.R. Gopidas and P.K. Das, *Chem. Phys. Lett.*, *167* (1990) 165.

[9] L.J. Johnston and D.F. Wong, *J. Phys. Chem.*, *97* (1993) 1589. L.J. Johnston and D.F. Wong, *Can. J. Chem.*, *70* (1992) 280.

[10] A. Azarani, A.B. Berinstain, L.J. Johnston and S. Kazanis, *J. Photochem. Photobiol. A*, *57* (1991) 175.

[11] D. Shukla and P. Wan, *J. Photochem. Photobiol. A*, *76* (1993) 47.

[12] R.E. Minto and P.K. Das, *J. Am. Chem. Soc.*, *111* (1989) 8858.

[13] M.K. Boyd, H.Y. Lai and K. Yates, *J. Am. Chem. Soc.*, *113* (1991) 7294.

[14] M.R. Valentino and M.K. Boyd, *J. Org. Chem.*, *58* (1993) 5826.

[15] M.R. Valentino and M.K. Boyd, *J. Photochem. Photobiol. A: Chem.*, *89* (1995) 7.

[16] J. McEwen and K. Yates, *J. Phys. Org. Chem.*, *4* (1991) 193.

[17] R.A. McClelland, N. Banait and S. Steenken, *J. Am. Chem. Soc.*, *111* (1991) 2929.

[18] D. Rehm and A. Weller, *Isr. J. Chem.*, *8* (1970) 259. D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, *73* (1969) 834.

[19] D. Shukla and P. Wan, *J. Photochem. Photobiol. A*, *79* (1994) 55.

[20] P. Wan, K. Yates and M.K. Boyd, *J. Org. Chem.*, *50* (1985) 2881.

[21] L.J. Johnston, J. Lobaugh and V. Wintgens, *J. Phys. Chem.*, *93* (1989) 7370.

[22] R.M. Berger and D. Weir, *Chem. Phys. Lett.*, *169* (1990) 213.

[23] L.M. Tolbert, S.M. Nesselroth, T.L. Netzel, N. Raya and M. Stapleton, *J. Phys. Chem.*, *96* (1992) 4492.

[24] G. Weber and F.W.J. Teale, *Trans. Faraday. Soc.*, *53* (1957) 646.

[25] V.M. Gomberg and L.H. Cone, *Justus Liebigs Ann. Chem.*, *376* (1910) 201.

[26] Y.-S. Ahn and J.-H. Shin, *Korean Chem. Soc.*, *26* (1982) 165.

[27] Y. Nagao, Y. Abe, T. Oyama, Y. Abe and T. Misono, *Nippon Kagaku Kaishi*, *10* (1987) 1839.

[28] H.J. Dauben, L.R. Honnen and K.M. Harmon, *J. Org. Chem.*, *25* (1960) 1442.

[29] S.J. Strickler and R.A. Berg, *J. Chem. Phys.*, *37* (1962) 814.

[30] N.J. Turro, *Modern Molecular Photochemistry*, Benjamin–Cummings, New York, 1978. J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry*, Wiley, New York, 1990.

[31] D. Meisel, P.K. Das, G.L. Hug, K. Bhattacharyya and R.W. Fessenden, *J. Am. Chem. Soc.*, *108* (1986) 4706.