

# Squaraine Photophysics in Polymer Films

Gary W. Scott\* and Kim Tran

Department of Chemistry, University of California, Riverside, Riverside, California 92521

Received: May 6, 1994; In Final Form: August 9, 1994\*

Absorption and emission spectra of four squaraine dyes—bis[4-(dimethylamino)phenyl]squaraine (H-Sq), bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine (HO-Sq), bis(trihydroxyphenyl)squaraine (3HO-Sq), and bis(azulyl)squaraine (Az-Sq)—are reported in dilute films of poly(methylmethacrylate) and polystyrene. Obtained for the first time are the fluorescence lifetimes of these dyes in these polymer films. Fluorescence lifetimes in liquid solutions are also reported. These emission kinetics combined with measurements of fluorescence quantum yields allow determination of radiative and nonradiative decay rate constants for three of the dyes. Comparison of determined radiative rate constants with those calculated from the absorption spectrum is consistent with the fluorescence originating from the absorbing species and state. The shortest lived fluorescence observed occurs for bis(trihydroxyphenyl)squaraine, and the short lifetime is attributed to either a rapid excited-state proton-transfer tautomerization or deprotonation. The  $S_1$  state of bis(azulyl)squaraine is nonfluorescent, presumably due to a rapid nonradiative decay similar to that which occurs in azulene. However, " $S_2$ "  $\rightarrow$   $S_0$  emission is observed for this azulyl-substituted squaraine.

## 1. Introduction

Squaraines (or squarylium dyes; see Figure 1) have been investigated for technological applications in xerography,<sup>1–3</sup> photovoltaics,<sup>4–6</sup> optical recording,<sup>7</sup> and nonlinear optics.<sup>8–12</sup> In particular, potential nonlinear optical device applications have investigated squaraine-doped polymers as candidate materials.<sup>8,9</sup> In addition, a spectral hole-burning study of squaraine dyes in several polymers has recently appeared.<sup>13</sup> We have also been investigating the  $\chi^{(3)}$  values in such systems and have therefore been prompted to investigate the photophysics of squaraine-doped polymers as reported in this work.

The molecular structure of squaraine consists of two donor moieties (D) connected to a central  $C_4O_2$  electron-withdrawing group (A). Both MNDO and CNDO calculations confirm this donor–acceptor–donor (D–A–D) arrangement in squaraine dyes.<sup>14</sup> Such calculations suggest that both the ground state and the lowest energy excited singlet state of squaraines involve significant intramolecular charge transfer (ICT), and thus the  $S_0 \rightarrow S_1$  electronic excitation may be labeled a CT transition. This CT process is primarily confined to the central  $C_4O_2$  unit.<sup>14</sup> The intramolecular charge-transfer character of this transition, combined with an extended conjugated  $\pi$ -electron donor network, yields a high molar extinction coefficient in the visible region of the spectrum for the squaraines.<sup>15</sup>

It has been suggested that in liquid solutions, solvent–solute complexes may form between squaraines and organic solute molecules.<sup>15</sup> Thus, multiple emission bands, identified for some squaraines in liquid solutions, have been assigned as emission from the excited state of a free squaraine, the excited state of a solute–solvent complex, and a twisted, relaxed excited state of these two forms.<sup>15–17</sup>

For an excited-state squaraine, it has been shown that internal rotation of the central  $C_4O_2$  unit promotes excited-state radiationless decay of some squaraines.<sup>15</sup> For example, bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine (HO-Sq; see Figure 1) has a higher fluorescence quantum yield and a longer fluorescence lifetime than does bis[4-(dimethylamino)phenyl]squaraine (H-Sq).<sup>18</sup> HO-Sq only differs from H-Sq by a

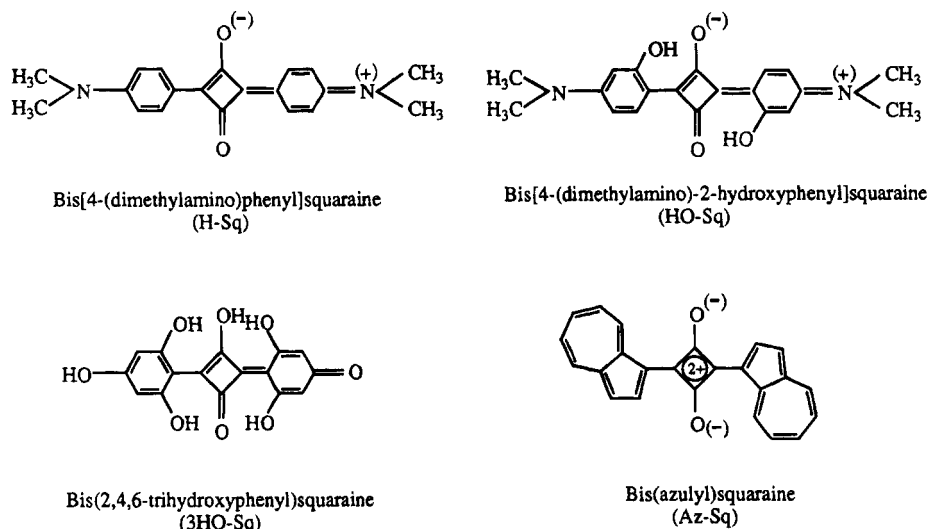
hydroxy group attached to each of the phenyl rings of the donor moieties (see Figure 1). Thus, since internal rotation of the central  $C_4O_2$  unit in HO-Sq is likely to be more restricted than it is in H-Sq due to intramolecular hydrogen bonds between the hydroxy groups and the central  $C_4O_2$  unit, internal rotation is implicated in the nonradiative decay.<sup>18</sup> Nevertheless, bis-(2,4,6-trihydroxyphenyl)squaraine (3HO-Sq), a squaraine with three hydroxy groups attached to each donor phenyl ring (see Figure 1), undergoes rapid nonradiative decay since, as previously reported,<sup>19</sup> fluorescence quantum yields and lifetimes of 3HO-Sq are significantly lower than those of either HO-Sq or H-Sq. Thus, some nonradiative decay process other than central ring rotation must be responsible for deactivation of the excited states of 3HO-Sq.

To elucidate the photophysical behavior of squaraine dyes in polymer films, we undertook the present study of H-Sq, HO-Sq, 3HO-Sq, and bis(azulyl)squaraine (Az-Sq, a previously uninvestigated squaraine). This paper presents spectroscopic information obtained for these squaraines in solid polymer films and, for comparison, in liquid solution, using steady-state spectroscopy and time-resolved fluorescence. Additional comparisons with previous spectroscopic studies of these dyes in liquid solutions<sup>11–23,47</sup> and polymer solutions<sup>13,23</sup> are also made. This work presents, for the first time, fluorescence lifetimes of squaraines measured in polymer films.

## 2. Experimental Section

**2.1. Materials.** H-Sq, HO-Sq, 3HO-Sq, and Az-Sq were prepared by following reported procedures.<sup>24</sup> For example, HO-Sq was synthesized by condensing one molecule of squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) with two molecules of 3-(dimethylamino)phenol. All solvents were spectrophotometric grade. Polymeric thin films incorporating different squarylium dyes were prepared by using both high molecular weight polystyrene (PS, MW = 250 000, Aldrich) and poly(methylmethacrylate) (PMMA, MW = 30 000, Aldrich), the latter having been purified by repeated reprecipitation and Soxhlet extraction as described earlier.<sup>25</sup> Films were cast from liquid solutions of the polymers and squaraine dyes, using either methylene chloride or ethyl acetate as the dissolving

\* Abstract published in *Advance ACS Abstracts*, October 1, 1994.



**Figure 1.** Molecular structures of bis[4-(dimethylamino)phenyl]squaraine (H-Sq), bis[4-(dimethylamino)-2-hydroxyphenyl]squaraine (HO-Sq), bis-(trihydroxyphenyl)squaraine (3HO-Sq), and bis(azulyl)squaraine (Az-Sq).

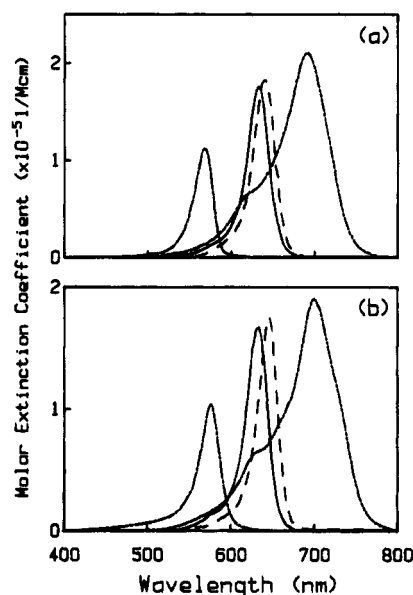
solvent for both polymer and dye. Typical film thicknesses were about 0.4 mm.

**2.2. Methods.** **2.2.1. Steady-State Absorption and Emission Spectroscopy.** All experiments were performed at room temperature. Prior to study, liquid solutions were deaerated by bubbling dry nitrogen gas through them, and solid polymer films were stored under vacuum at least for 12 h just prior to study. Absorption spectra were obtained using a Varian DMS 100s UV–visible spectrophotometer in a double-beam configuration. Steady-state emission spectra were recorded with a spectrofluorimeter (Spex Fluorolog, Model F212). Schott KV non-fluorescing filters were used to eliminate scattered excitation light. Emission intensities were quantum counter ratioed to the excitation beam intensity and corrected for wavelength variation of the detector efficiency. All emission spectra were base line corrected with blank solvent or host polymer spectra. Fluorescence quantum yields of liquid solutions were measured by the optically dilute relative method,<sup>26</sup> using 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4*H*-pyran (DCM in dimethyl sulfoxide,  $\phi_f = 0.71$ )<sup>27</sup> as a standard. For squaraines in thin polymer films (PMMA and polystyrene), fluorescence quantum yields were obtained with a technique developed to determine emission quantum yields of powdered samples.<sup>28,29</sup>

**2.2.2. Emission Kinetics.** The fluorescence kinetics were measured using an excitation pulse from a mode-locked Nd<sup>3+</sup> glass laser system (second harmonic at 532 nm, ~10 ps pulse width). The time-resolved fluorescence intensity profile was monitored at 90° with respect to excitation through nonfluorescing filters and a polarizer set at the “magic angle” of 54.7°. The fluorescence signal was detected by a streak camera (Hamamatsu C979), which had been triggered, with an appropriate timing delay, by a portion of the fundamental laser pulse. A portion of the second harmonic laser pulse was directed to the streak camera as a timing marker to arrive shortly before the sample fluorescence signal. Streak traces including the marker pulse plus the time-resolved fluorescence profile were imaged onto a two-dimensional Vidicon detector (512 × 512 channels, EG&G PARC Model 1216 controller and Model 1215 processor) for subsequent analysis. Further details of data analysis, including the deconvolution technique, have been published elsewhere.<sup>30,31</sup>

### 3. Results

**3.1. Steady-State Absorption and Emission Spectra.** Figure 2 shows the visible-region absorption spectra of H-Sq, HO-



**Figure 2.** Room-temperature absorption spectra, obtained with a 1 nm bandpass, of (a) squaraines in PMMA, H-Sq (—), HO-Sq (---), 3HO-Sq (·····), and Az-Sq (— · — ·) and (b) squaraines in PS, H-Sq (—), HO-Sq (---), 3HO-Sq (·····), and Az-Sq (— · — ·).

Sq, 3HO-Sq, and Az-Sq when doped into polymer films. These molecules show similar spectroscopic behavior as they do in dilute liquid solution at room temperature.

Except for Az-Sq, all squaraine dyes in polymer matrices exhibit fluorescence in the visible region with detectable emission quantum yields. Figure 3 shows the emission spectra of squaraines in PMMA and polystyrene matrices. These spectra are scaled to their relative fluorescence quantum yields.

For Az-Sq, although no detectable  $S_1 \rightarrow S_0$  fluorescence was observed, it is relatively easy to detect emission from an upper singlet state of the molecule after exciting in the UV. This emission, superimposed on a UV–visible absorption spectrum of Az-Sq in methylene chloride, is shown in Figure 4.

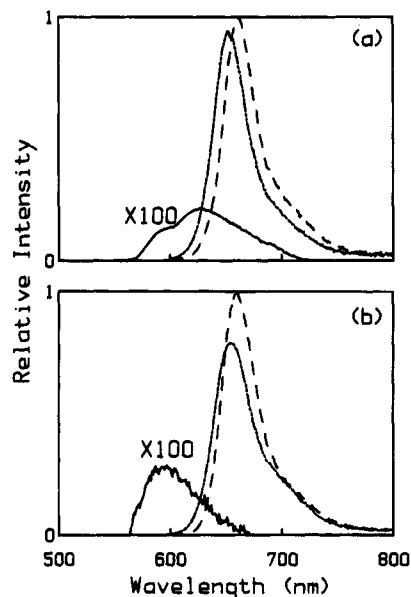
Table 1 summarizes the steady-state absorption and emission spectral results for the squaraines studied, both in polymer films and, for comparison, in liquid solutions. Fluorescence quantum yields, measured in this work, are also included in Table 1.

**3.2. Emission Kinetics.** Typical time-resolved emission profiles of HO-Sq in a liquid solution and of H-Sq in PMMA,

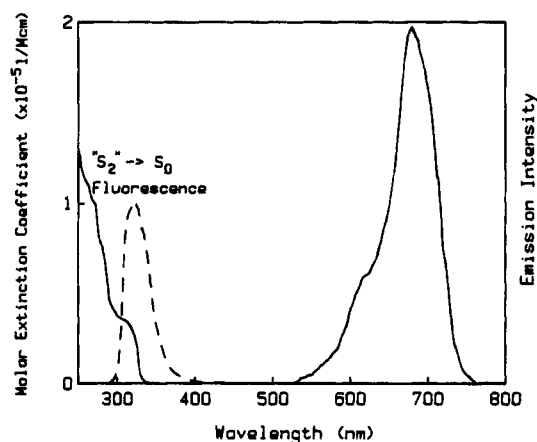
**TABLE 1: Room-Temperature, Steady-State Spectroscopic Results and Fluorescence Kinetics in the Visible Region for Three Squaraines**

squaraine	solvent <sup>a</sup> or polymer host <sup>b</sup>	absorption $\lambda_{\text{max}}$ (nm)	$\epsilon$ (l mol <sup>-1</sup> cm <sup>-1</sup> )	emission $\lambda_{\text{max}}$ (nm)	$\phi_f$	$\tau_f$ (ns)
H-Sq	PMMA	626	$1.8 \times 10^5$	651	$0.57 \pm 0.15$	$2.62 \pm 0.64$
	PS	632	$1.7 \times 10^5$	653	$0.79 \pm 0.13$	$5.19 \pm 0.23$
	CH <sub>2</sub> Cl <sub>2</sub>	629	$2.6 \times 10^5$	651	$0.36 \pm 0.16$	$1.31 \pm 0.38$
HO-Sq	PMMA	636	$1.8 \times 10^5$	662	$0.68 \pm 0.12$	$3.08 \pm 0.71$
	PS	644	$1.8 \times 10^5$	660	$0.87 \pm 0.09$	$5.43 \pm 0.64$
	CH <sub>2</sub> Cl <sub>2</sub>	638	$3.0 \times 10^5$	659	$0.54 \pm 0.12$	$1.90 \pm 0.40$
3HO-Sq	PMMA	567	$1.1 \times 10^5$	626, 590 (sh)	$0.0017 \pm 0.0010$	$0.013 \pm 0.001$
	PS	576	$1.0 \times 10^5$	597	$0.0019 \pm 0.0009$	$0.013 \pm 0.006$
	C <sub>2</sub> H <sub>5</sub> OH	510	$1.3 \times 10^5$	610	$0.0020 \pm 0.0010$	$0.012 \pm 0.003$

<sup>a</sup> Liquid solvents: CH<sub>2</sub>Cl<sub>2</sub> = methylene chloride; C<sub>2</sub>H<sub>5</sub>OH = ethanol. <sup>b</sup> Solid polymers: PMMA = poly(methylmethacrylate); PS = polystyrene.

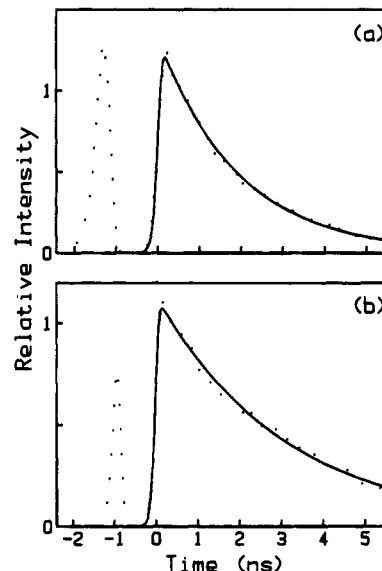


**Figure 3.** Room-temperature emission spectra ( $\lambda_{\text{ex}} = 532$  nm) of (a) squaraines in PMMA, 3HO-Sq (—), HO-Sq (---), and H-Sq (· · · · ·) and (b) squaraines in PS, 3HO-Sq (—), HO-Sq (---), and H-Sq (· · · · ·).



**Figure 4.** Absorption (—) and steady-state “S<sub>2</sub>” → S<sub>0</sub> emission (---,  $\lambda_{\text{ex}} = 280$  nm) spectra of Az-Sq/CH<sub>2</sub>Cl<sub>2</sub> at room temperature. (“S<sub>2</sub>” is a higher energy singlet state of Az-Sq analogous to the S<sub>2</sub> state of azulene).

obtained with a 532 nm excitation pulse, are shown in Figure 5. All such decay profiles were least-squares fitted with a single-exponential function including simultaneous deconvolution of the laser excitation pulse. For H-Sq and HO-Sq, the fluorescence lifetimes are a few nanoseconds. For 3HO-Sq, however, the fluorescence lifetime both in liquid solution and in solid polymer blends is much shorter, on the order of 10 ps.



**Figure 5.** (a) Time-resolved fluorescence profile at room temperature,  $\lambda_{\text{ex}} = 532$  nm, of HO-Sq/CH<sub>2</sub>Cl<sub>2</sub>. (b) Time-resolved fluorescence profile at room temperature,  $\lambda_{\text{ex}} = 532$  nm, of H-Sq in PMMA. The dots are the experimental data points. The solid line represents the single-exponential least-squares fit. The prepulse signal, as shown, is the timing marker for signal averaging.

For Az-Sq, no emission corresponding to the S<sub>1</sub> → S<sub>0</sub> transition was detected. The measured lifetimes are given in Table 1.

#### 4. Discussion

There have been several previous reports of the electronic absorption spectra of H-Sq,<sup>15,18,23,32</sup> HO-Sq,<sup>15,18,21,23</sup> and 3HO-Sq.<sup>19,20,33</sup> The spectrum of Az-Sq has not been previously reported. These squaraines exhibit strong, sharp absorption bands in the visible region (Figures 2 and 4). Semiempirical MNDO and CNDO molecular orbital calculations suggest that both the S<sub>0</sub> and S<sub>1</sub> states of these molecules possess significant charge separation.<sup>14</sup> In addition, these calculations show that charge transfer, essentially confined to the central C<sub>4</sub>O<sub>2</sub> moiety, is involved in S<sub>0</sub> → S<sub>1</sub> electronic excitation in these systems. Thus, the lowest energy absorption band corresponding to this transition should not be strongly perturbed by variation of the donating groups attached to the C<sub>4</sub>O<sub>2</sub> ring. However, as shown in Figure 2, the wavelength of this absorption band is nevertheless somewhat dependent upon the donor structure. For example, the molecular structure of H-Sq differs from that of 3HO-Sq by a *p*-dimethylamino substituent on each of the donor phenyl rings in place of three symmetrically distributed hydroxy groups on each. This substituent difference results in a red shift of the maximum of the lowest energy absorption band of H-Sq by ~60 nm from that of 3HO-Sq (see Figure 2). This effect is likely due to the presence of better electron-donating

**TABLE 2: Radiative and Nonradiative Rate Constants of Squaraines in Liquid Solutions, PMMA, and Polystyrene at Room Temperature**

squaraine	liquid solutions			PMMA		polystyrene	
	$k_{nr}(\times 10^{-8})$ (s <sup>-1</sup> )	$k_r(\times 10^{-8})$ (s <sup>-1</sup> )	$k_r^{cal}(\times 10^{-8})$ (s <sup>-1</sup> )	$k_{nr}(\times 10^{-8})$ (s <sup>-1</sup> )	$k_r(\times 10^{-8})$ (s <sup>-1</sup> )	$k_{nr}(\times 10^{-8})$ (s <sup>-1</sup> )	$k_r(\times 10^{-8})$ (s <sup>-1</sup> )
H-Sq	4.89 ± 2.59 <sup>a</sup>	2.75 ± 1.46 <sup>a</sup>	3.48 ± 0.30	1.64 ± 0.59	2.18 ± 0.78	0.40 ± 0.07	1.52 ± 0.26
HO-Sq	2.42 ± 0.74 <sup>b</sup>	2.84 ± 0.87 <sup>b</sup>	2.83 ± 0.20	1.04 ± 0.30	2.20 ± 0.64	0.24 ± 0.04	1.60 ± 0.25
3HO-Sq	792 ± 439 <sup>c</sup>	1.59 ± 0.88 <sup>c</sup>	2.04 ± 0.18	751 ± 438	1.31 ± 0.77	750 ± 477	1.44 ± 0.91

<sup>a</sup> H-Sq/CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> HO-Sq/CH<sub>2</sub>Cl<sub>2</sub>. <sup>c</sup> 3HO-Sq/C<sub>2</sub>H<sub>5</sub>OH.

*p*-dimethylamino groups at favorable positions for enhancing charge delocalization over the entire molecule.

The absorption spectra of the squaraines studied in PMMA and PS are quite similar to those obtained in liquid solution (see Figure 2 and Table 1). Absorption and emission maxima as well as extinction coefficients in liquid solutions are similar to previous reports to the extent that similar solvents were used.<sup>15,18,19,21,22</sup> The large extinction coefficients and narrow bandwidths are consistent with the D-A-D CT character of the S<sub>0</sub> → S<sub>1</sub> absorption. Extinction coefficients are slightly lower for HO-Sq and H-Sq in the polymer hosts than in liquid solutions (see Table 1), as are radiative rate constants (see Table 2). However, the latter differences are with experimental error. Fluorescence excitation line-narrowing spectra and nonpersistent hole-burning experiments of a squaraine with a structure closely related to HO-Sq in a hydrogen-bonding polymer host at liquid helium temperatures were recently reported.<sup>13</sup> These experiments reveal vibronic structure which is otherwise hidden by inhomogeneous broadening in ordinary absorption spectra.<sup>13</sup>

Our spectra indicate that the intermolecular interactions amongst the dye molecules, such as those that occur in neat thin films,<sup>1,4</sup> are absent for these molecules embedded within rigid polymer matrices. Furthermore, no significant perturbations of the dye molecules by the polymer matrices are evident from these spectra. By way of contrast, the absorption spectra of amorphous neat thin films of the squaraines fail to exhibit the characteristic strong, sharp visible absorption band.<sup>1,4</sup> Instead, a very broad, red-shifted absorption is observed over the entire visible region. Extensive intermolecular interactions resulting from aggregation are likely responsible for the broad spectra of the neat thin films.<sup>2,3,23</sup>

The spectral emission bands of squaraines are also sensitive to the molecular structure of the donor substituents. Relatively narrow, structureless emission bands were detected for H-Sq and HO-Sq, in polymer films as in liquid solution (see Figure 3 and Table 1). The peak of the HO-Sq emission band exhibits a small red shift, ~10 nm, compared with that of H-Sq, similar to the shift observed for the corresponding absorption spectra.

Both H-Sq and HO-Sq emit strongly in polymer films as well as in liquid solutions at room temperature.<sup>15</sup> (Our measured quantum yields for these two squaraines in methylene chloride are slightly lower than those previously reported,<sup>15</sup> but not significantly so.) In addition, their emission band positions and shapes are quite similar in both liquid solutions and the solid matrices (see Table 1). The emission quantum yields,  $\phi_f$ , of H-Sq and HO-Sq are slightly higher in PMMA and polystyrene than in liquid solution (see Table 1). 3HO-Sq, on the other hand, does not emit strongly in any solution, and its emission characteristics are solvent sensitive.

A previous investigation<sup>15</sup> of squaraines in liquid solution reported that their emission spectra consist of as many as three emission bands, designated as  $\alpha$ ,  $\beta$ , and  $\gamma$ . These three spectral bands of squaraine were assigned, respectively, to emission from a Franck-Condon excited-state dye molecule, an excited state of the dye complexed with a solvent cage, and a relaxed twisted excited (TICT) state of the molecule.<sup>15</sup> Three distinct emission

bands were not observed in the spectra of these squaraines in polymer films at room temperature (see Figure 3). If a TICT state were formed as a result of an internal rotation of the C—C linkages between the central C<sub>4</sub>O<sub>2</sub> unit and the phenyl rings, its formation should be more favorable in liquid solution than in the more rigid polymeric matrices. Perhaps the lack of resolved emission bands in the polymers is due to additional inhomogeneous broadening in the polymer hosts. Transient absorption studies, on the excited singlet states of H-Sq and HO-Sq, do not provide evidence to support the existence of the multiple forms of excited singlet state squaraines, again perhaps because of the broad spectra involved.<sup>18</sup>

The time-resolved emission profiles, obtained for H-Sq, HO-Sq, and 3HO-Sq in liquid solutions and in solid polymer films, were analyzed by fitting the decays with first-order kinetics. As presented in Table 1, the lifetimes obtained as the best fit parameters to the decay curves are in the nanosecond to picosecond range. For liquid solutions, the fluorescence lifetimes we obtain are in reasonably good agreement with excited-state lifetimes obtained from transient absorption kinetics.<sup>18</sup> As shown in Figure 5, the profiles for H-Sq and HO-Sq are well fitted by single-exponential decay functions. Thus, in each case, it is reasonable to assign only one excited singlet state of a single species as responsible for the observed emission decays.

The fluorescence quantum yields and fluorescence lifetimes are generally higher for squaraines in solid polymeric matrices than their corresponding values in liquid solutions, as shown in Table 1. The observed fluorescence decay rate constant,  $k = 1/\tau_f$ , is controlled by  $k = k_r + k_{ISC} + k_{IC}$ , where  $k_r$  is the radiative rate constant,  $k_{ISC}$  is the rate constant for the intersystem crossing, and  $k_{IC}$  is the rate constant for the internal conversion, all for the decay of the S<sub>1</sub> state. Both H-Sq and HO-Sq are known to have low intersystem crossing efficiencies ( $\phi_{ISC} < 0.001$ ),<sup>18</sup> so  $k_{IC} \approx k_{nr}$ , the total nonradiative decay rate constant. Thus,  $k_r = \phi_f/\tau_f$ , and  $k_{nr} = (1 - \phi_f)/\tau_f$ . Both  $k_r$  and  $k_{nr}$  for squaraines in liquid solutions and in polymeric matrices were thereby calculated and are presented in Table 2. Although the values of  $k_r$  are about the same for H-Sq, HO-Sq, and 3HO-Sq, the value of  $k_{nr}$  is significantly larger for 3HO-Sq than for the other two. (Variation in the values of  $k_r$  reported in Table 2 are within experimental error and should not be considered significant.)

The radiative decay rates of H-Sq, HO-Sq, and 3HO-Sq were also calculated by integrating the lowest energy absorption band for the liquid solution data using the Strickler-Berg relationship.<sup>34</sup>

$$k_r^{cal} = (2.880 \times 10^{-9}) n^2 \langle \bar{\nu}_f^{-3} \rangle_{Av}^{-1} \int \epsilon d \ln \bar{\nu} \quad (1)$$

in which  $n$  is the refractive index,  $\langle \bar{\nu}_f^{-3} \rangle_{Av}$  is the mean value of the inverse-cubed wavenumber (in cm<sup>-1</sup>) of the fluorescence spectrum, and the integral of  $\epsilon$  (the molar extinction coefficient) is taken over the S<sub>0</sub> → S<sub>1</sub> absorption band.

Since there is a significant separation between the S<sub>0</sub> → S<sub>1</sub> and S<sub>0</sub> → S<sub>2</sub> transition bands for these three molecules, the

lowest energy absorption band of each spectrum was integrated directly without further deconvolution. The resulting values of  $k_r^{\text{cal}}$  are included in Table 2. For H-Sq, HO-Sq, and 3HO-Sq, as shown in Table 2, the radiative decay rates,  $k_r$ , obtained from  $k_r = \phi_f/\tau_f$ , are in reasonably good agreement with the values of  $k_r^{\text{cal}}$ .

For a large number of squaraines, a rapid intramolecular twisting of the central  $\text{C}_4\text{O}_2$  moiety has been proposed as a mechanism which promotes radiationless excited-state decay.<sup>15</sup> Thus, the nonradiative excited-state decay of squaraines should be inhibited by decreasing the rate of this intramolecular twisting. Methods to do so include hydrogen bonding between the donor moieties and the oxygen atoms on the central ring or increased rigidity of the microenvironment surrounding the squaraine molecules.

Thus, the decrease of the nonradiative decay rates of H-Sq and HO-Sq in solid polymeric thin films as compared to those of liquid solutions which we have observed (see Table 2) may be attributed to the more rigid microenvironments provided by the polymers. Furthermore, the nonradiative decay rate of HO-Sq, as given in Table 2 and previously noted,<sup>18,47</sup> is somewhat lower than that of H-Sq in both liquids and polymer films. This difference may be attributed to the presence of a hydroxy group at the ortho position of each aromatic donor moiety in HO-Sq to form intramolecular hydrogen bonds between these hydroxy groups and the polar oxygen atoms of the central ring. Such hydrogen bonds would be expected to hinder the intramolecular twisting, thus lowering the nonradiative excited-state decay rate of HO-Sq.

The photophysics of 3HO-Sq is clearly different from that of H-Sq or HO-Sq in both liquid solution and solid polymer films (see Tables 1 and 2). Recently, Das et al. have reported the emission and absorption spectra of 3HO-Sq in methanol/water solutions<sup>20</sup> both with and without poly(4-vinylpyridine) (P4VP), complexed with  $\beta$ -cyclodextrin ( $\beta$ -CD) in aqueous solutions,<sup>19</sup> and in acetonitrile.<sup>33</sup> Their results may be summarized, in part, as follows: (1) only the singly deprotonated species  $3\text{HO-Sq}^-$  emits with a significant quantum yield ( $\phi_f \geq 0.01$ ) in methanol/water solutions;<sup>19,20</sup> (2) complexing of 3HO-Sq with  $\beta$ -CD<sup>19</sup> or P4VP<sup>20</sup> results in an increase in the fluorescence quantum yield up to  $\phi_f \sim 0.2$ ; and (3) J-type aggregates of 3HO-Sq may form in acetonitrile, on the basis primarily of evidence provided by absorption spectral changes with 3HO-Sq concentration.

The increase in the fluorescence quantum yield of 3HO-Sq in aqueous solutions containing  $\beta$ -CD was attributed by Das et al.<sup>19</sup> to the formation of a 1:1 inclusion complex of the 3HO-Sq with the  $\beta$ -CD. They argued that encapsulation of the 3HO-Sq molecules with a  $\beta$ -CD cavity prevents the formation of intermolecular hydrogen bonds with the solvent. Thus, a more "rigidized" excited-state molecule forms in the  $\beta$ -CD complex with intramolecular hydrogen bonds between the ortho hydroxy groups and the oxygen atoms of the central ring.<sup>19</sup> In the case of 3HO-Sq complexes with P4VP in methanol/water solutions, these authors argue that intermolecular H-bonds with the P4VP polymer also rigidize the 3HO-Sq moiety, increasing its fluorescence quantum yield.<sup>20</sup>

In the present work, we find that the fluorescence quantum yield of 3HO-Sq at room temperature is quite low ( $\phi_f \sim 0.002$ ; see Table 1) and is virtually unchanged upon going from liquid solution (ethanol, an H-bonding solvent) to solid polymer films (PMMA and PS). The polymer environments should be quite rigid and, at least in the case of PS, non-hydrogen-bonding.<sup>13</sup> Thus, it seems that neither the rigidity of the 3HO-Sq nor its environment is a strong influence on  $k_{\text{nr}}$  (see Table 2). It seems

likely to us that the nonradiative deactivation of excited-state 3HO-Sq is due to a mechanism such as intramolecular proton transfer or deprotonation.

For some organic molecules which have phenolic hydroxyl groups adjacent to a carbonyl group such as hydroxybenzophenones<sup>35</sup> or hydroxyflavones,<sup>36</sup> hydrogen bonds to the carbonyl oxygen are established in the ground state. Relatively large Stokes shifts and rapid nonradiative decays observed for these molecules upon their electronic excitation have been attributed to an excited-state intramolecular proton-transfer process resulting in tautomerization.<sup>35-38</sup>

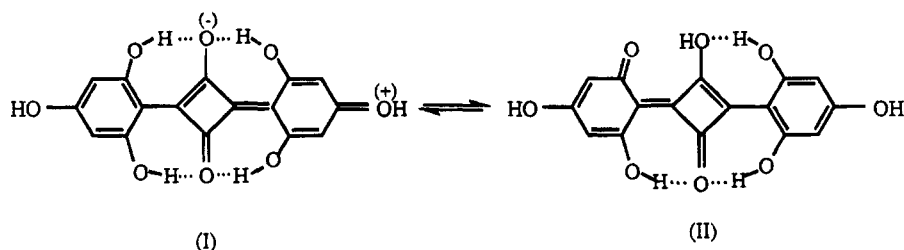
Due to the similarity in the molecular structure of 3HO-Sq and those of substituted hydroxyflavones or hydroxychromes,<sup>36,37</sup> it seems plausible that intramolecular hydrogen bonds may be formed in ground-state 3HO-Sq. One possible ground-state hydrogen-bonded configuration (I) of 3HO-Sq is shown in Figure 6a. The fluorescence lifetimes measured for 3HO-Sq in either liquid ethanol solution or solid polymeric thin films are all less than 15 ps and considerably shorter than those obtained for H-Sq and HO-Sq (see Table 1). The fluorescence Stokes shift, defined as the energy difference of the band peaks of the absorption and emission spectra in wavenumbers is quite variable for 3HO-Sq at room temperature:  $\sim 3200\text{ cm}^{-1}$  in ethanol,  $\sim 1700\text{ cm}^{-1}$  in PMMA, and only  $\sim 500\text{ cm}^{-1}$  in PS. Conversely, the Stokes shifts for HO-Sq and H-Sq are all only a few hundred wavenumbers. Furthermore, the fluorescence of 3HO-Sq in PMMA is distinctive, consisting of two bands, a peak at 626 nm and a shoulder at  $\sim 590\text{ nm}$  (see Table 1 and Figure 3).

The low quantum yields, short lifetimes, and environment-dependent Stokes shifts suggest that for 3HO-Sq rapid excited-state, intramolecular proton transfer or even deprotonation of 3HO-Sq may promote its radiationless internal conversion. A possible tautomerization of 3HO-Sq is shown in Figure 6a. As analogous examples, hydroxybenzophenones<sup>35</sup> and substituted benzothiazoles<sup>39</sup> undergo ultrafast nonradiative excited-state decay for similar reasons, resulting in fluorescent lifetimes of less than 100 ps.<sup>35,38,40</sup>

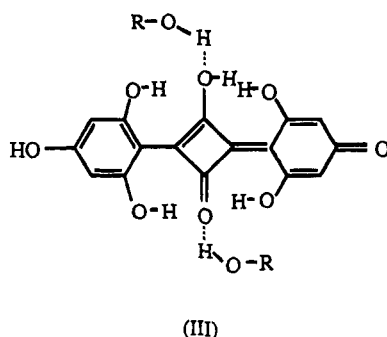
In many cases, the excited-state proton-transfer processes are highly solvent dependent. The lack of a detectable emission from 3HO-Sq in chlorinated hydrocarbon solvents, as previously mentioned, may be due to an even more rapid excited-state proton transfer. In alcoholic solutions, however, a possible ground-state structure (III) of 3HO-Sq as shown in Figure 6b may be formed. The intermolecular hydrogen bonds as shown in III may assist in removing or partially disrupting the intramolecular hydrogen bonds as shown in I. The rate of  $\text{I} \rightarrow \text{II}$  tautomerization may then be reduced. As a result, the nonradiative decay rate of 3HO-Sq may decrease to the extent that the emission of 3HO-Sq becomes detectable. This interpretation is analogous to the one suggested to explain the slowing of the excited-state decay rate in alcoholic solutions as observed for 2-(2'-hydroxy-5'-methylphenyl)benzotriazole<sup>38</sup> and 3-hydroxyflavone.<sup>41</sup> For 3HO-Sq doped into PMMA or into polystyrene, the rigidized matrices at room temperature may also assist in reducing the rate of proton transfer in the excited state. As a result, emission is also observed for 3HO-Sq in PMMA or polystyrene at room temperature.

For HO-Sq, its structure suggests that an intramolecular hydrogen-bonded configuration may also be formed in its ground state. However, the Stokes shift, as mentioned above, for HO-Sq is relatively small ( $\sim 500\text{ cm}^{-1}$ ), and its fluorescence lifetime is significantly longer than that of 3HO-Sq. It is likely therefore that the rate of excited-state proton transfer is significantly slower for HO-Sq, probably due to a relatively high

a.



b.



**Figure 6.** (a) Possible ground-state (I) and excited-state (II) molecular structures of 3HO-Sq in aprotic solvents. (b) Plausible ground-state structure (III) of 3HO-Sq in alcoholic solvent.

energy barrier for its tautomerization, and does not contribute significantly to its excited-state decay.

Thus, in addition to an intramolecular rotation of the central  $C_4O_2$  unit, it is possible that excited-state proton transfer and tautomerization or deprotonation may play an important role in the nonradiative deactivation process of 3HO-Sq. However, further independent evidence is needed to elucidate the relative importance that each nonradiative mechanism contributes to deactivation of the excited state of this molecule.

The report of Das et al.<sup>33</sup> that 3HO-Sq forms J-type aggregates in acetonitrile deserves some comment. We have confirmed that, in this solvent, the absorption spectrum of 3HO-Sq in the visible region consists of two bands, centered at 480 and 563 nm. The higher energy band was assigned in the previous work to the absorption of a monomeric species of 3HO-Sq, while the lower energy band, observed only at relatively higher concentrations of the dye, was assigned to absorption by a dimeric J-type aggregate form of 3HO-Sq in acetonitrile.<sup>33</sup> The assignment of the lower energy band to a J-type dimer is, in our view, open to question. We have determined that the intensity of the band at 480 nm in acetonitrile is enhanced by water contamination of the acetonitrile. Acetonitrile is a solvent which is notoriously difficult to dry. In solvents more easily obtained in anhydrous form (e.g., dichloroethane), we found that the 480 nm band is absent at *all* 3HO-Sq concentrations. Thus, the 480 nm band could also be assigned to a 3HO-Sq/ $H_2O$  complex in monomeric form with the 563 nm band due to either a J-aggregate or an uncomplexed monomer. The water complex would only form at low concentrations, comparable to the water impurity level in the acetonitrile, while the other band would grow at higher concentrations.

No room-temperature emission was detected from Az-Sq upon electronic excitation to its lowest energy excited singlet state. However, as shown in Figure 4, an intense near-UV emission was observed from a sample of Az-Sq in liquid solution at room temperature upon its excitation into a higher energy electronic excited state. Although a technical violation of Kasha's rule,<sup>42</sup> this " $S_2$ "  $\rightarrow$   $S_0$  emission is similar to the anomalous  $S_2 \rightarrow S_0$  emission observed for azulene and other substituted azulenes.<sup>43–45</sup> For Az-Sq, the relatively large " $S_2$ " -  $S_1$  energy difference ( $\Delta E/hc \sim 9000\text{ cm}^{-1}$ ) is similar to that in azulene,<sup>44</sup> making the nonradiative " $S_2$ "  $\rightsquigarrow$   $S_1$  decay process slower than in most molecules. Further, emission from the  $S_1$  state of azulene upon direct excitation is not readily observed due to a fast nonradiative intersystem crossing process to the nearby  $T_1$  state.<sup>46</sup> A similar situation results for Az-Sq, thus accounting for the total absence of  $S_1 \rightarrow S_0$  emission of Az-Sq at room temperature.

## 5. Conclusions

From our spectroscopic investigation of several squaraines in polymer films at room temperature, it is apparent that their photophysical behavior is highly influenced by the molecular structure of the electron-donating groups attached to the central  $C_4O_2$  moiety. A further influence is the chemical and physical nature of the surrounding environments. Comparison with studies in liquid solutions indicates that the fluorescing states and photophysics of squaraines are quite similar to those in the polymer films. Amongst the four squaraines studied, HO-Sq has been found to have highest fluorescence quantum yield and lowest nonradiative decay rate constant. The shortest lived

excited  $S_1$  states belong to 3HO-Sq and, presumably even shorter, to Az-Sq. The former decays rapidly due to an excited-state proton-transfer tautomerization or deprotonation but still exhibits an observable short-lived  $S_1 \rightarrow S_0$  fluorescence. The latter exhibits no such observable  $S_1 \rightarrow S_0$  emission, presumably decaying even more rapidly by intersystem crossing and/or internal conversion.

**Acknowledgment.** We wish to thank Dr. Seth Marder of the California Institute of Technology Beckman Institute for generously providing some of the squarines for this study. K.T. acknowledges the stipend support of a California Space Institute Fellowship. This research was supported by an INCOR Grant from the Center for Nonlinear Studies at Los Alamos National Laboratory and by the Committee on Research at the University of California, Riverside.

## References and Notes

- Wingard, R. E. *IEEE Ind. Appl.* **1982**, 1251.
- Law, K.-Y.; Bailey, F. C. *J. Imaging Sci.* **1987**, 31, 172.
- Law, K.-Y. *J. Phys. Chem.* **1988**, 92, 4226.
- Merritt, V. Y. *IBM J. Res. Dev.* **1978**, 22, 353.
- Morel, D. L.; Ghosh, A. K.; Feng, T.; Stogryn, E. L.; Purwin, P. E.; Shaw, R. F.; Fishman, C. *Appl. Phys. Lett.* **1978**, 32, 495.
- Morel, D. L.; Stogryn, E. L.; Ghosh, A. K.; Feng, T.; Purwin, P. E.; Shaw, R. F.; Fishman, C.; Bird, G. R.; Piechowski, A. P. *J. Phys. Chem.* **1984**, 88, 923.
- Gravestijn, D. J.; Steenbergen, C.; van der Veen, J. *Proc. SPIE Int. Soc. Opt. Eng.* **1983**, 420, 327.
- Dirk, C. W.; Kuzyk, M. G. *Chem. Mater.* **1990**, 2, 4.
- Kuzyk, M. G.; Paek, U. C.; Dirk, C. W. *Appl. Phys. Lett.* **1991**, 59, 902.
- Chen, C. T.; Marder, S. R.; Cheng, L. T. *J. Chem. Soc., Chem. Commun.* **1994**, 259.
- Chen, C. T.; Marder, S. R.; Cheng, L. T. *J. Am. Chem. Soc.* **1994**, 116, 3117.
- Yu, Y. Z.; Shi, R. F.; Garito, A. F.; Grossman, C. H. *Opt. Lett.* **1994**, 19, 786.
- Vanthey, E.; Voss, J.; DeCaro, C.; Renn, A.; Wild, U. P. *J. Lumin.* **1993**, 56, 61.
- Bigelow, R. W.; Freund, H. J. *Chem. Phys.* **1986**, 107, 159.
- Law, K.-Y. *J. Phys. Chem.* **1987**, 91, 5184.
- Law, K.-Y. *J. Phys. Chem.* **1989**, 93, 5925.
- Law, K.-Y. *Chem. Phys. Lett.* **1992**, 200, 121.
- Kamat, P. V.; Das, S.; Thomas, K. G.; George, M. V. *J. Phys. Chem.* **1992**, 96, 195.
- Das, S.; Thomas, K. G.; George, M. V.; Kamat, P. V. *J. Chem. Soc., Faraday Trans.* **1992**, 88, 3419.
- Das, S.; Kamat, P. V.; De la Barre, B.; Thomas, K. G.; Ajayaghosh, A.; George, M. V. *J. Phys. Chem.* **1992**, 96, 10327.
- Kamat, P. V.; Das, S.; Thomas, S. G.; George, M. V. *Chem. Phys. Lett.* **1991**, 178, 75.
- Law, K.-Y. *J. Imaging Sci.* **1990**, 34, 38.
- Law, K.-Y. In *Photophysics of Polymers*; ACS Symposium Series 358; American Chemical Society: Washington, DC, 1987; p 301.
- Sprenger, H. E.; Ziegenbein, W. *Agnew. Chem., Int. Ed. Engl.* **1968**, 7, 530.
- Iannone, M. A.; Scott, G. W.; Brinza, D.; Coulter, D. R. *J. Chem. Phys.* **1986**, 85, 4863.
- Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, 75, 991.
- Hammond, P. R. *Opt. Commun.* **1979**, 29, 331.
- Wrighton, M. S.; Ginley, D. S.; Morse, D. L. *J. Phys. Chem.* **1974**, 78, 2229.
- O'Connor, D. B.; Scott, G. W.; Coulter, D. R.; Yavrouian, A. J. *Phys. Chem.* **1991**, 95, 10252.
- O'Connor, D. B.; Scott, G. W.; Coulter, D. R.; Miskowski, V. M.; Yavrouian, A. J. *J. Phys. Chem.* **1990**, 94, 6495.
- O'Connor, D. B.; Scott, G. W.; Coulter, D. R.; Yavrouian, A. *Macromolecules* **1991**, 24, 2355.
- Loutfy, R. O.; Hsiao, C. K.; Kazmaier, P. M. *Photogr. Sci. Eng.* **1983**, 27, 5.
- Das, S.; Thanulingam, L.; Thomas, K. G.; Kamat, P. V.; George, M. V. *J. Phys. Chem.* **1993**, 97, 13620.
- Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, 37, 814.
- Merritt, C.; Scott, G. W.; Gupta, A.; Yavrouian, A. *Chem. Phys. Lett.* **1980**, 69, 169.
- Kasha, M. *J. Chem. Soc., Faraday Trans.* **1986**, 82, 2379.
- McMorrow, D.; Kasha, M. *J. Am. Chem. Soc.* **1983**, 105, 5133.
- Huston, A. L.; Scott, G. W.; Gupta, A. *J. Chem. Phys.* **1982**, 76, 4978.
- Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1980**, 102, 5631.
- McMorrow, D.; Dzugas, T. P.; Aartsma, T. J. *Chem. Phys. Lett.* **1984**, 103, 492.
- McMorrow, D.; Kasha, M. *J. Phys. Chem.* **1984**, 88, 2235.
- Kasha, M. *Discuss. Faraday Soc.* **1950**, 9, 14.
- Beer, M.; Longuet-Higgins, H. C. *J. Chem. Phys.* **1955**, 23, 1390.
- Viswanath, G.; Kasha, M. *J. Chem. Phys.* **1956**, 24, 574.
- Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, 78, 125.
- Nickel, B. *Chem. Phys. Lett.* **1979**, 68, 17.
- Rehak, V.; Israel, G. *Chem. Phys. Lett.* **1986**, 132, 236.