

Squaraine Chemistry. Effects of Structural Changes on the Absorption and Multiple Fluorescence Emission of Bis[4-(dimethylamino)phenyl]squaraine and Its Derivatives

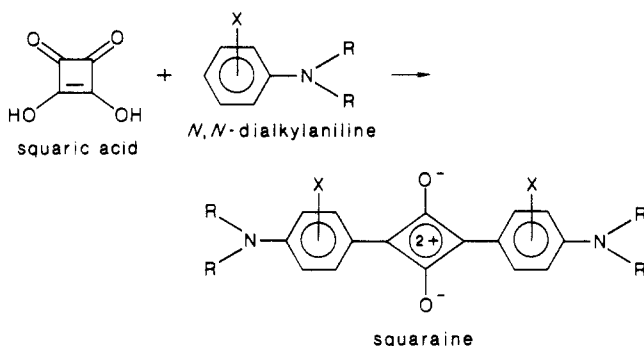
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The absorption and the steady-state fluorescence emission of a class of donor-acceptor-donor (D-A-D) molecules, bis-[4-(dimethylamino)phenyl]squaraine and its derivatives (**1-19**), have been studied. Squaraines generally exhibit intense solution absorption in the red ($\epsilon \sim 3 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$). All substituents studied in this work exert a bathochromic effect on the absorption. The effect is small and is attributable to the minor involvement of the donor group in the $S_0 \rightarrow S_1$ excitation. In conjunction with emission data, we are able to show that the bathochromic shift originates from the solute-solvent complex and that the complexation constant increases as the D-A-D charge-transfer character of squaraine increases. Electronic and steric factors affecting the D-A-D character and subsequently the absorption maximum are discussed in terms of the solute-solvent complex model. Multiple-emission bands are observed in the fluorescence spectra of **1-19**. Three bands, α , β , and γ , are identified from their typical Stokes shifts. Controlled experiments showed that the multiple-emission bands are intrinsic emissive properties of squaraines. Results from mixed-solvent experiments, solvent-effect studies, and temperature-effect studies show that squaraines form solute-solvent complexes in organic solvents. A photophysical model to account for the multiple emission is proposed. Excitation of squaraine in solution results in two excited states, namely, the excited state of free squaraine and the excited state of the solute-solvent complex. These two excited states emit photons to give the α -emission and the β -emission. Rotational relaxation(s) (around the C-C bond between the phenyl ring and the four-membered ring of squaraine) is (are) shown to be the major radiationless decay process(es) of these two excited states. As a result, a twisted relaxed excited state is generated. This relaxed excited state can undergo a rotational relaxation to the ground state or emit a photon to give the γ -emission. The effect of structural changes on the multiple emission is discussed.

Introduction

Bis[4-(dimethylamino)phenyl]squaraine (**1**) and its derivatives are 1,3-disubstituted products synthesized from squaric acid and *N,N*-dialkylanilines.¹ The synthesis of squaraines is simple and



has been reviewed several times in the literature.² Although squaraines exhibit sharp visible absorption in solution, their absorption in the solid state is panchromatic (400-1000 nm) and is usually very intense.³ These features have made them very attractive for various technological applications in industry, e.g., xerographic photoreceptors,⁴ organic solar cells,^{3,5} and optical recording media.⁶ While the technological uses of these com-

pounds have been extensive and a large number of squaraines have been synthesized,⁷ reported electronic spectral data have been limited only to a few absorption spectra.^{3,8} The general spectroscopic properties of squaraines are practically unexplored.

The ground-state and the excited-state electronic structures of **1** have recently been studied by Bigelow and Freund using MNDO and CNDO semiempirical molecular-orbital approximations.⁹ These authors showed that the electronic distribution of **1** is highly polarized, with the anilino moiety being an electron donor (D) and the central C_4O_2 unit being an electron acceptor (A). The localized charges at the nitrogen, the oxygen, and the central C_4O_2 unit in the ground state are approximately -0.4 e, -0.35 e, and +0.37 e, respectively. They further showed that there is a charge transfer (CT) during the $S_0 \rightarrow S_1$ electronic excitation but that the CT is primarily confined in the central C_4O_2 unit (0.094 e from each oxygen atom to the four-membered ring). Although there is a small degree of CT from the anilino moiety to the C_4O_2 unit, the degree of CT is relatively minor (0.019 e from D to C_4O_2). In any event, MO calculations suggest that both S_0 and S_1 states of squaraine are intramolecular D-A-D CT states. The effect of this symmetric D-A-D arrangement on the general spectroscopic properties of intramolecular charge-transfer states is an interesting subject of fundamental investigation. Here we report the absorption and the fluorescence emission spectra of squaraines **1-19** (structures shown in Table I). The effects of structural changes on the electronic spectra will be presented and discussed.

Experimental Section

Materials. Squaraines were synthesized from squaric acid and *N,N*-dialkylaniline derivatives according to the procedure described by Sprenger and Ziegenbein.^{8b} Satisfactory spectroscopic and analytical data were obtained for all the compounds studied and were reported earlier.^{10,11} Solvents were either of spectro grade

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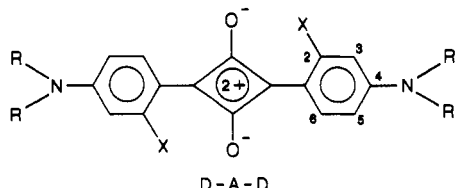
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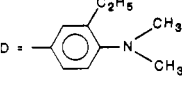
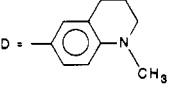
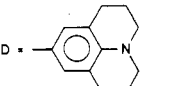
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TABLE I: Effect of Substituent on the Absorption Spectra of Squaraines (in Methylene Chloride)



squaraine	substituent	λ_{\max} , nm	$\log \epsilon$, $\text{cm}^{-1} \text{M}^{-1}$
1	R = CH ₃ , X = H	627.6	5.49
2	R = C ₂ H ₅ , X = H	634.1	5.51
3	R = C ₃ H ₇ , X = H	638.8	5.53
4	R = C ₄ H ₉ , X = H	640.0	5.53
5	R = C ₁₈ H ₃₇ , X = H	641.8	5.52
6	R = CH ₃ , X = CH ₃	643.5	5.42
7	R = C ₂ H ₅ , X = CH ₃	651.0	5.49
8	R = C ₄ H ₉ , X = CH ₃	657.1	5.47
9	R = CH ₃ , X = OCH ₃	631.8	5.40
10	R = C ₂ H ₅ , X = OCH ₃	638.8	5.48
11	R = C ₄ H ₉ , X = OCH ₃	643.5	5.51
12	R = CH ₃ , X = OH	635.9	5.52
13	R = C ₂ H ₅ , X = OH	641.1	5.57
14	R = C ₄ H ₉ , X = OH	648.2	5.56
15	R = CH ₃ , X = F	630.0	5.09
16	R = CH ₃ , X = C ₂ H ₅	643.0	5.40
17		628.8	5.11
18		645.0	5.50
19		661.0	5.53

from Fisher or of analytical grade from Baker; they were routinely stored over 3-Å molecular sieves before use.

General Techniques. Absorption spectra were recorded with a Cary 17 spectrophotometer. Fluorescence spectra were taken on a Perkin-Elmer MPF 44A spectrofluorometer which was equipped with a differential corrected spectra unit (DCSU-2). A 1,1,2-trichloroethane solution of tetra-*tert*-butyl metal-free phthalocyanine ($\sim 1 \times 10^{-3}$ M) was used in place of the RhB quantum counter solution so that corrected excitation and fluorescence spectra could be obtained up to 750 nm. Fluorescence quantum yields were determined (in a corrected mode) by comparing with the emission of sulforhodamine 101 in ethanol ($\phi_f = 1.0$),¹² and a refractive index correction was made for each solvent.¹³

Results and Discussion

Squaraines exhibit intense and sharp absorption bands in the visible region. Their absorption maxima (λ_{\max}) vary from 627 to 661 nm, depending on the substituent at the nitrogen and the

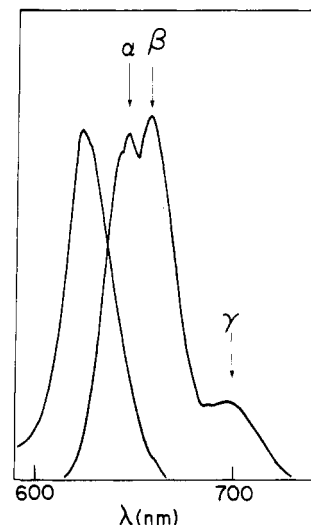


Figure 1. Corrected fluorescence excitation and emission spectra of 1 in CH₂Cl₂ ([1] $\sim 3 \times 10^{-7}$ M).

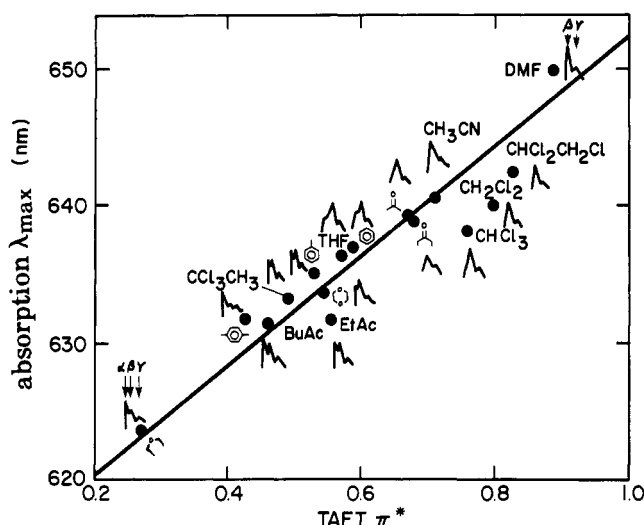


Figure 2. Plot of λ_{\max} of 4 as a function of solvent parameter π^* .

substituent in the phenyl ring. The absorption spectral data of squaraines 1–19 in methylene chloride solution are summarized in Table I.

1. Effect of *N*-Alkyl Groups. The results in Table I show that λ_{\max} of squaraines 1–5 (X = H) shifts to the red by 12.4 nm, accompanied with a slight, but consistent, increase in ϵ as the length of the *N*-alkyl chain increases. This trend is also seen in three other series of squaraines, namely, 6–8 (X = CH₃), 9–11 (X = OCH₃), and 12–14 (X = OH) where red-shifts of 13.6, 12, and 12.2 nm, respectively, are observed. The small bathochromic shift observed in these compounds is consistent with the MO calculation results by Bigelow and Freund, who showed that the charge transfer during the optical excitation is primarily confined in the central C₄O₂ unit. Nevertheless, MO calculations also showed that there is a small increase in positive charge (0.019 e) at each nitrogen atom upon excitation. Although the small shift can be attributed to an inductive charge stabilization of the excited D–A–D CT state by the *N*-alkyl group, we consider it unlikely because if charge stabilization is a big factor for the bathochromic shift, we should have observed a large effect in 12–14 due to the strong electron-releasing hydroxyl groups. We observe the contrary experimentally. The bathochromic effect exerted by an *N*-alkyl group is larger than that by a hydroxy group (Table I).

As shall be seen in the emission spectra of 1–5 (Figures 1 and 5), there is a gradual dominance of emission from the solute-solvent complex as the length of the *N*-alkyl group increases. Since MO calculations suggested that there would be an increase in

(11) Characterization data of 5, 11, and 14 were not reported in ref 10 and are summarized as follows: 5, mp 110–113 °C; ¹H NMR (CD₂Cl₂) δ 0.7–1.9 (m, 14 H), \sim 3.4 (t, 8 H), 6.80 (d, *J* = 9.5 Hz, 4 H), 8.30 (d, *J* = 9.5 Hz, 4 H). Anal. Calcd for C₈₈H₁₅₆N₂O₂: C, 82.95; H, 12.34; N, 2.20. Found: C, 83.02; H, 12.18; N, 1.97. 11, mp 90–93 °C; ¹H NMR (CDCl₃) δ 0.96 (t, *J* = 7 Hz, 12 H), 1.1–1.8 (m, 16 H), 3.42 (t, *J* = 6.9 Hz, 8 H), 3.97 (s, 6H), 6.05 (d, *J* = 9.5 Hz, 2 H), 6.2–6.4 (m, 2 H), 8.48 (d, *J* = 9.5 Hz, 2 H). Anal. Calcd for C₃₄H₄₈N₂O₄: C, 73.81; H, 8.52; N, 5.38. Found: C, 73.65; H, 9.05; N, 4.89. 14, mp 193–195 °C; ¹H NMR (CDCl₃) δ 0.97 (t, *J* = 5 Hz, 12 H), 1.08–1.9 (m, 16 H), 3.38 (t, *J* = 8 Hz, 8 H), 6.09 (d, *J* = 2.2 Hz, 2 H), 6.3 (ABq *J*_A = 9.4 Hz, *J*_B = 2.2 Hz, 2 H), 7.88 (d, *J* = 9.4 Hz, 2 H). Anal. Calcd for C₃₂H₄₄N₂O₄: C, 73.81; H, 8.52; N, 5.38. Found: C, 73.73; H, 8.37; N, 5.26.

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D-A-D CT character when the polarized charges are stabilized,⁹ the observed bathochromic shift may be attributable to the formation of solute-solvent complexes due to the increase in D-A-D CT character as the length of the *N*-alkyl group increases. This proposition is supported by the results on the solvent-effect study of **4** where analogous trends in the absorption and emission spectra are observed when the D-A-D structure of **4** is polarized by polar solvents (see results in Figure 2).

2. Effect of C-2 Substituents. Substituents at C-2 generally produce bathochromic effects on the absorption λ_{\max} (Table I). The red-shifts are very small (2–16 nm), however, and are attributable to the minor involvement of the D moiety in the CT excitation.⁹ The special feature of the results lies in the relative magnitude of the red-shift observed in these compounds. Since the excited state of squaraine is a D-A-D CT state, it is intuitively expected that the red-shift should increase as the electron-donating (-releasing) ability of the substituent at C-2 increases. Accordingly, the expected order of red-shift should be: $\text{CH}_3\text{O} \sim \text{OH} > \text{F} > \text{CH}_3 \sim \text{C}_2\text{H}_5$. Experimentally, a reversed order is observed. The red-shifts of **9**, **12**, **15**, **6**, and **16** (relative to **1**) are 4.2, 8.3, 2.4, 15.9, and 15.4 nm, respectively.

In addition to the relatively large red-shifts, a decrease in ϵ is also observed in **6–8** and **16**. Since it is known in the literature that the absorption coefficient of a CT state would decrease as the CT interactions between the D-A moiety decrease,¹⁴ the decrease in ϵ in **6–8** and **16** suggests that there is a decrease in D-A-D CT interactions in these squaraines. We propose that, due to the steric repulsion between the C-2 alkyl group and the C-O group, **6–8** and **16** become nonplanar, leading to a reduction of CT interactions. This nonplanarity results in a nonplanar ground-state, nonplanar excited-state (lower energy) electronic transition. The relative large bathochromic shift observed in these compounds is thus a conformational effect. This hypothesis also gains support from our emission data, where we observe a significant decrease in the fluorescence quantum yields of **6–8** and **16** owing to the facile rotational relaxation of the already twisted excited state of these compounds.

The λ_{\max} of **12–14** is red-shifted by ~ 8 nm from those of **1–4**, and the red-shift is about 2 times smaller than those of **6–8** ($\text{X} = \text{CH}_3$). The small red-shift observed despite having a strong electron-releasing group (OH) in the D moiety further illustrates the minor role of the D moiety in the electronic excitation. The ϵ values of **12–14** are in the range of $(3.3\text{--}3.5) \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ and are about 10% higher than those of **1–4**. These high ϵ values, which are in contrast to the low values of **6–8**, suggest that **12–14** are planar molecules despite the C-2 substitution. The planarity is presumably the result of the H-bonding between the C-2 hydroxy groups in the phenyl ring and the C-O groups in the four-membered ring. Thus, the red-shift observed in **12–14** can be attributed to the CT stabilization of the positive charge in the D moiety in the excited state.

The λ_{\max} of **9–11** is red-shifted by 4–5 nm from those of **1–4**. Since the electron-releasing properties between a methoxy group and a hydroxy group are very similar, the smaller red-shifts observed in **9–11** are somewhat unexpected. Incidentally, smaller ϵ values $[(2.5\text{--}3.2) \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}]$ are observed in **9–11**. These results suggest that, as in the cases of **6–8** and **16**, the phenyl ring and the four-membered ring of **9–11** may be twisted from planarity by steric repulsion. The smaller red-shift in **9–11** is thus attributable to the decrease of CT stabilization by the D moiety in the excited state.

Fluorine substitution at C-2 is expected to give interesting results because of its σ electron-withdrawing nature and π electron-releasing nature. The λ_{\max} of **15** red-shifts by 2.4 nm from that of **1**. Since an electron-withdrawing group is expected to produce a blue-shift on the λ_{\max} , the observed red-shift is indicative of CT stabilization in the excited state. The ϵ value of **15** is $1.5 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ and is ~ 2.5 times less than that of **1**. While twisting

around the C-C bond between the phenyl ring and the four-membered ring is expected, the degree of twisting in **15** is expected to be smaller than those in **6–11**. Thus, twisting alone cannot account for the small ϵ value in **15**. Very similar decreases in ϵ and small red-shifts on λ_{\max} are also observed for a number of fluoro-*N*-benzylsquaraines.¹⁵ At present, we cannot offer any satisfactory explanation for these results.

3. Effect of C-3 Substituents. Very interesting substituent effects are observed for squaraines with C-3 substituents. In case of **17**, ethyl substitution at C-3 results in a very small red-shift of the λ_{\max} (1.2 nm). This is a factor of >12 smaller than that of **16** when the C-2 position is substituted and may be due to the small CT stabilization effect at C-3 because positive charges of the CT state are primarily localized at the C-2 and the C-6 positions in the phenyl ring. The ϵ value of **17** is $\sim 1.28 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ and is significantly lower than that of **1**. The lowering in ϵ may be attributed to the lack of delocalization of the lone-pair electrons at the nitrogen to the π -orbital of squaraine due to the twisting of the C-N bond induced by the steric repulsion between the ethyl and the *N,N*-dimethylamino groups. The mechanism of the decrease in ϵ in **17** is analogous to that of **6–11**.

When the C-3 substituent is structurally linked to the *N,N*-dialkylamino group, such as in **18** and **19**, relatively large red-shifts on the λ_{\max} , 17.4 nm for **18** and 33.4 nm for **19**, are observed. The ϵ values of **18** and **19** are $(\sim 3.1\text{--}3.4) \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ and are comparable to those of **1–4**. Since **18** and **19** exhibit primarily solute-solvent complex emission in methylene chloride, the large bathochromic shift is ascribable to the formation of the solute-solvent complex. The shift in equilibrium of complex formation in the cases of **18** and **19** is probably due to the extensive delocalization of the lone-pair electrons at the nitrogen to the π -orbital enabled by the increased rigidity in the *N,N*-dialkylamino group, which subsequently enhances the D-A-D CT character of **18** and **19** in the ground state. The mechanism of enhancing the CT character in the ground states of **18** and **19** is very similar to those provided by the electron-releasing *N*-alkyl groups and by polar solvents.

Fluorescence Emission

1. Emission Spectrum of 1. Figure 1 shows the fluorescence excitation and emission spectra of **1** in methylene chloride. The excitation spectrum was found to be independent of the monitoring wavelengths and was identical with the absorption spectrum. Three emission bands at λ_F 646, 660, and ~ 702 nm are observed. These three bands are designated as the α -, the β -, and the γ -bands from their Stokes shifts, which are typically in the range of 200–400, 530–780, and 1400–1700 cm^{-1} from the absorption λ_{\max} , respectively. Although purification of **1** by recrystallization techniques is difficult, attempts were made to purify **1** by different washing schemes. We observed no change either in the absorption or in the emission spectrum after extensive solvent washings. Further experiments were also pursued to study the effect of purification on the absorption and the emission of squaraine with a soluble squaraine, **4**, as a model. Results show that both absorption and emission spectra of **4** are unaffected quantitatively after solvent recrystallization or chromatographic purification. We thus conclude that the multiple emission observed in Figure 1 is not caused by any impurity in the squaraine sample.

The multiple emission of **1** is also found not due to any emissions from the dimer, the excimer, or any aggregational states of **1**. For instance, most of the absorption spectra reported in Table I were recorded at $<5 \times 10^{-5} \text{ M}$ and Beer's Law was found to obey for all the squaraine solutions studied. Emission spectra were studied at a squaraine concentration of $<3 \times 10^{-7} \text{ M}$. Controlled experiments (using **1**, **4**, **6**, **9**, **12**, and **15**) showed that the shape of the emission band and the quantum yield of the emission remain unaffected when the original squaraine solution was diluted (by a factor of 2 and 5). Our results lead us to conclude that the multiple emission in Figure 1 is an intrinsic emissive property of **1**.

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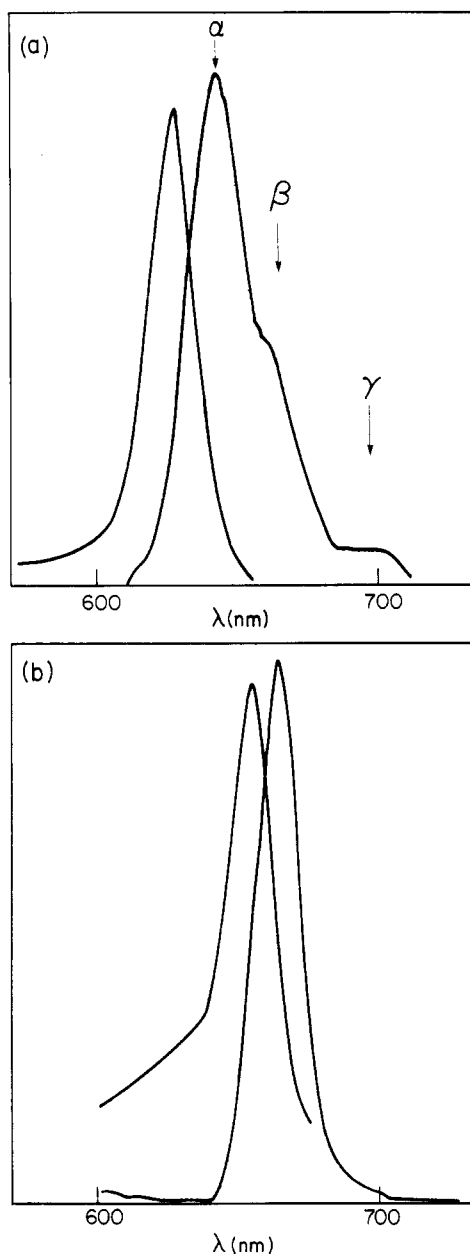


Figure 3. Corrected fluorescence excitation and emission spectra of **4** in ether (a) at 298 K and (b) at 77 K (concentration $\sim 5 \times 10^{-7}$ M).

2. *On the Origin of the α - and the β -Emissions.* Probable explanations for the multiple emission of **1** are (a) vibronic fine structure of the emission band, (b) emission from a relaxed excited state, or (c) emission from an exciplex (with solvent) or an excited state of some kind of solute-solvent complex. In order to differentiate these possibilities, the effects of solvent, temperature, and structural changes on the multiple-emission bands were studied. Major evidence for the spectral assignment of the γ -emission comes from the structural effect study of **6–8**, and the results will be discussed in a later section. Here we concentrate on evidence for the elucidation of the origin of the α -emission and the β -emission. Squaraine **4** was chosen as a model compound for our solvent- and temperature-effect studies because of its high solubility in various solvents. The relative intensity of the α -emission and the β -emission is found to be solvent and temperature sensitive, and the results are discussed in terms of a solute-solvent complexation model. The proposed model is substantiated by studying the electronic spectra of **4** in a mixture of solvent (ether/chloroform) where isosbestic point and isoemissive point are observed in the absorption and the emission spectra of **4**, respectively.

Effect of Solvent. Results in Figure 2 show that the absorption λ_{\max} of **4** undergoes a bathochromic shift as the solvent parameter

TABLE II: Effect of Substituent on the Fluorescence Spectra of Squaraines (in Methylene Chloride).

squaraine	λ_F , nm			ϕ_f^a	$\phi_\gamma/\phi_f, \%$
	α	β	γ		
1	~ 646	~ 660	~ 702	0.65	11
2	650 ^c	660	~ 702	0.69	12
3	651 ^c	662.5	~ 702	0.70	14
4		664	~ 705	0.70	13
5		664.5	~ 705	0.74	11
6		669.5	~ 706	0.023	27
7		671.5	~ 705	0.036	34
8		675	~ 705	0.054	40
9	650 ^c	661 ^c	~ 704	0.042	18
10		665	~ 702	0.049	29
11		664	~ 704	0.26	17
12	650 ^c	660	~ 704	0.86	11
13		661.5	~ 705	0.86	12
14		665	~ 702	0.83	12
15	652 ^c	661.5	~ 701	0.091	17
16		669.5	~ 705	0.024	40
17	638	650	~ 704	0.42	12
18		666.5	~ 701	0.45	10
19		680	~ 705	0.32	50

^a Total fluorescence quantum yield, estimated error $\pm 5\%$. ^b ϕ_γ/ϕ_f , contribution of the γ -emission to the total fluorescence, estimated error $\sim \pm 20\%$. ^c Shoulder.

π^* increases, and this is accompanied with a change in the composition of the emission spectra (see inset in Figure 2). For example, in diethyl ether (Figure 3a), the emission spectrum of **4** is dominated by the α -band with λ_F at 641 nm. The excitation spectrum is independent of the monitoring wavelength and is identical with the absorption spectrum. Because of the good overlap and mirror-image relationship between the absorption spectrum and the emission spectrum, the spectral result in Figure 3a suggests that the α -band is from a Franck-Condon excited state of **4**. An emission shoulder at λ_F 660 nm and a small band at λ_F 698 nm are also seen in Figure 3a, and these two emission bands are assigned to the β -band and the γ -band according to their Stokes shifts. If one assumes that the multiple emission is due to fine vibrational structures, the α -band and the β -band would be from the (0,0) and (0,1) transitions, respectively. From the splitting between the α -band and the β -band in Figure 3a as well as the data in Table II, the γ -band would be the (0,3) transition. The (0,2) transition, which is expected to be ~ 675 nm in Figure 3a, is missing. Careful inspection of the emission spectra of **1–19** in CH_2Cl_2 , as well as those of **4** in over 30 solvents, fail to identify any emission band or shoulder corresponding to the (0,2) transition. Solvents are known to affect the relative intensity of vibrational bands in aromatic hydrocarbons. Notable examples are the effects of solvent on the absorption fine structure of benzene (Ham effect)¹⁶ and the effect of solvent on the relative intensity of the fine structure in the fluorescence emission of pyrene.¹⁷ The variation in intensity of the α -, β -, and γ -bands as the structure of squaraine and the solvent vary may well be vibrational in nature. However, the persistent absence of the (0,2) transition in over 50 emission spectra recorded in our laboratory seems to make such an assignment suspicious.

Major evidence against the vibronic structure assignment comes from the specific solvent effects observed in alcoholic solvents. The λ_{\max} of **4** is found to depart from the λ_{\max} vs. π^* relationship in Figure 2 in alcoholic solvents. Instead, λ_{\max} shifts to longer wavelengths as the steric hindrance around the hydroxy group decreases; e.g., λ_{\max} is ~ 634.1 nm in tertiary amyl alcohol, ~ 639.4 nm in secondary alcohols, and 642.6 ± 0.2 nm in primary alcohols. In conjunction with the bathochromic shift, an accompanied increase in intensity for the β -band is observed. The correlation between the bathochromic shift of the absorption λ_{\max} and the

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increase in emission intensity of the β -band of **4** in alcohols is identical with that seen in Figure 2. The significance of the results in alcohols lies in the steric dependence (rather than π^* dependence) of both λ_{\max} and emission composition. Very similar short-range interactions between the excited state of *p*-(dimethylamino)benzonitrile (DMABN) and alkyl amines was reported by Wang¹⁸ recently, where he reported that the rate of quenching of the fluorescence emission of DMABN by alkyl amines is steric sensitive due to the formation of an exciplex. The similar steric dependence observed in the electronic spectra in this work suggests that the interactions between **4** and alcoholic solvent molecules are also short range. We propose that **4** forms solute-solvent complexes in alcoholic solvents and the complexation site is around the OH group.¹⁹ As the steric hindrance around the OH group decreases, solute-solvent complexation increases, resulting in the bathochromic shift of λ_{\max} and an increase in β -emission intensity. The general solvent effect on the λ_{\max} and the emission composition of **4** (Figure 2) suggests that the complexation process is very general and complexation becomes very pronounced in solvents of $\pi^* > 0.65$. Accordingly, the α -band is the Franck-Condon emission of the excited state of the solute and the β -band is the Franck-Condon emission of the excited state of the solute-solvent complex.

Effect of Temperature. An additional experiment in favor of the solute-solvent complex model comes from the low-temperature electronic spectra of **4** in ether. Squaraine **4** exhibits an absorption at λ_{\max} of 654 nm and a single emission at λ_F 664 nm at 77 K in ether matrix (Figure 3b). The observation of a bathochromic shift in the emission spectrum is certainly against general expectation from vibrational fine structures where a hypsochromic shift of λ_F should be obtained.²⁰ Controlled experiments show that the low-temperature spectra are not due to any aggregation because identical excitation and emission spectra can be obtained when the concentration of **4** in the matrix is decreased (by a factor of 10) and because very similar spectral results are obtained when a better solvent (2-MeTHF) is used.

The substantial shift of the absorption (32 nm) at 77 K should not be due to the increase in solvency as the temperature is lowered. Although the π^* value of ether at 77 K is not known, the dielectric constant of ether at 77 K can be estimated to be ~ 15 according to its temperature dependence.²¹ From the scattered relationship between λ_{\max} of **4** and the solvent dielectric constant, one can estimate that λ_{\max} of **4** at 77 K in ether matrix would be 638 ± 2 nm if the bathochromic shift is purely a solvency shift. The anomalously large shift leads us to conclude that the absorption is from the solute-solvent complex and that its formation is probably a temperature stabilization effect. Since the excitation spectrum at 77 K is identical with the absorption spectrum and shows good overlap and mirror-image relationship with the emission spectrum, the single emission at λ_{\max} 664 nm can be assigned to the Franck-Condon emission of the solute-solvent complex. Since a solvent effect study of **4** shows that λ_F is relatively insensitive toward increasing solvent polarity (e.g., $\lambda_F\beta \sim 660$ nm in ether, $\lambda_F\beta = 665$ nm in acetonitrile), by comparison of the spectral data in Figure 3, we can conclude that the β -emission at room temperature is an emission from the solute-solvent complex. The α -emission is an emission from the excited state of the solute. This deduction is identical with that obtained from the solvent-effect study.

Another significant finding in the low-temperature emission spectrum is the absence of the γ -emission at ~ 700 nm. As shown in a later section, emission data of **6-8** suggest that the γ -emission

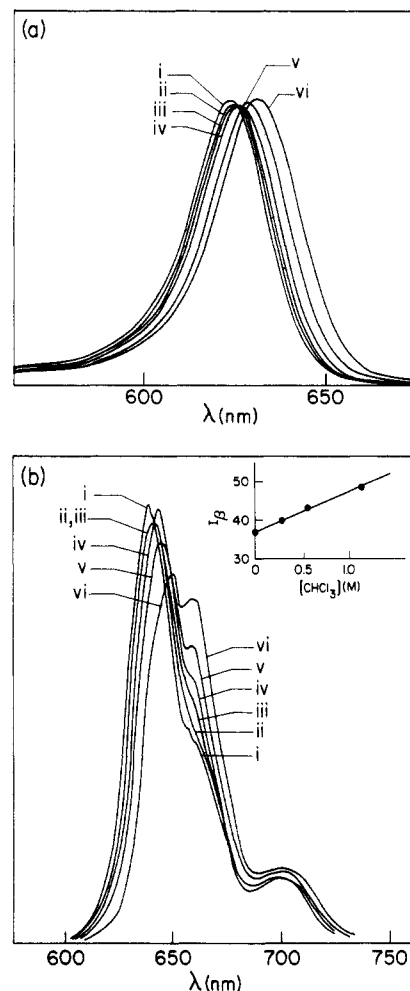


Figure 4. Effect of chloroform concentration on (a) absorption and (b) corrected fluorescence spectra of **4** in ether [$[\text{CHCl}_3] =$ (i) 0, (ii) 0.28, (iii) 0.56, (iv) 1.12, (v) 2.24, and (vi) 4.48 M].

is derived from a relaxed, twisted excited state. Its absence at low temperature is thus consistent with the model proposed below, simply implying that the relaxation process, which involves a C-C bond rotation, is prohibited at 77 K.

Mixed Solvent Experiments. If the above assignment of the α -band and the β -band was correct, **4** exists primarily as free squaraine species in diethyl ether, and addition of a complexing solvent in an ether solution of **4** should increase the concentration of the solute-solvent complex. As a result, both λ_{\max} and λ_F should shift to the red and the β -emission should increase. Such an experiment is, however, complicated by the fact that most complexing solvents are more polar than ether. Addition of a complexing solvent in ether not only induces complexation but also increases the dielectric constant (ϵ) of the medium, which is also known to affect the complexation process. In order to circumvent this dilemma, we performed our experiments in a ternary system, namely, ether ($\epsilon = 4.43$), chloroform ($\epsilon = 4.7$), and *n*-hexane ($\epsilon = 1.9$). The addition of *n*-hexane in the mixture is to keep ϵ constant as the concentration of chloroform varies. Results in Figure 4 show that λ_{\max} and λ_F shift to the red as $[\text{CHCl}_3]$ increases at $[\text{CHCl}_3] \leq 1.12$ M. Simultaneously, an *isosbestic point* at ~ 625 nm and an *isoemissive point* at ~ 662 nm are observed. The observation of an isosbestic point in the absorption spectra and an isoemissive point in the emission spectra is very indicative of the formation of complex between **4** and CHCl_3 in ether and provides further evidence that the β -emission is indeed from the excited state of the solute-solvent complex and the α -emission is from the excited state of free squaraine in solution. The stoichiometry of the complex is found to be 1:1 at $[\text{CHCl}_3] < 1.12$ M as indicated in the plot of the intensity of the β -emission (I_β) vs. $[\text{CHCl}_3]$ (see inset of Figure 4b). The complexation

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constant between **4** and chloroform cannot be determined, however, due to the close overlapping of the α - and β -emissions.

Further bathochromic shifts on the λ_{\max} and the λ_F and further increases in I_β are observed at $[\text{CHCl}_3] \geq 2.24 \text{ M}$. Absorption curves and emission curves are not longer passed through their isosbestic or isoemissive points. This observation can be attributed either to the preferred solvation of the solute-solvent complex by chloroform as the concentration of chloroform increases or to the formation of a 1:n solute-solvent complex. The occurrence of these two events is presumably due to the highly localized concentration of chloroform in the solvation shell of squaraine, a consequence of the solute-solvent complexation process.

In summary, from the short-range and specific solvent effects observed in alcoholic solvents, the isosbestic point and the isoemissive point observed in the electronic spectra of **4** in the mixed-solvent experiments, and the low-temperature spectra of **4** in ether matrix, we conclude that squaraines form complexes with solvent molecules in the ground state as well as the excited state, which in turn generate the α -emission and the β -emission observed in this work.

Complexation processes between solvent molecules and compounds having intramolecular charge-transfer states are known. For example, Wang²² observed very similar solute-solvent complexation in the ground state and the excited state in his study of the photophysics of polarized enones. Wang¹⁸ recently also reported a study of the exciplex formation between DMABN and alkyl amines where a steric effect on the exciplex formation was observed. The steric effect reported in Wang's paper is actually analogous to the (ROH:4) complex in this work. In a similar context, Varma and co-workers^{23,24} reported extensive evidence for the exciplex formation between DMABN and polar solvent molecules. In one of their papers, Visser and Varma²³ actually demonstrated the formation of a 1:1 exciplex between DMABN and alkylnitrile in cyclohexane using a mixed-solvent experiment analogous to that reported in this work. The dipole moment of the excited state of DMABN is $\sim 14 \text{ D}$.²⁵ Assuming that the polarized charges in the excited state are localized in the dimethylamino group and the cyano group, each of these groups will bear $\sim 0.42 \text{ e}$ of opposite charges. The formation of an exciplex is presumably due to interactions between these polarized charges and the dipoles of solvent molecules. As pointed out in the Introduction, the polarized charges in the ground state of squaraine **1** are -0.35 e at the oxygen atoms, $+0.37 \text{ e}$ in the four membered ring and approximately, -0.4 e at the nitrogen atoms. Thus, interactions between the polarized charges in squaraines with dipoles of the solvent molecules are really not irrational. In fact, complexation processes of squaraines with solvent molecules are not unprecedented. For example, Merritt²⁶ reported the preparation of a high concentration (up to $\sim 10^{-2} \text{ M}$) of **12** in ethylene diamine and propylamine. The amine solution was "straw-colored" and did not show any normal squaraine absorption in the red. Squaraine **12**, however, can be regenerated when the amine solvent is evaporated. Merritt concluded the high solubility of **12** in amine solvents (10^{-2} M as compared to $<10^{-5} \text{ M}$ in organic solvents) to the formation of a solute-solvent complex. Yanus²⁷ recently found that this complexation process is very general and the pigment regeneration process can be used as a means of purifying squaraine pigments. Complexation between squaraines and polar species have also been observed in the vapor phase. For example, we observed a very general complexation process between squaraines and anilino fragments in our recent mass spectrometric

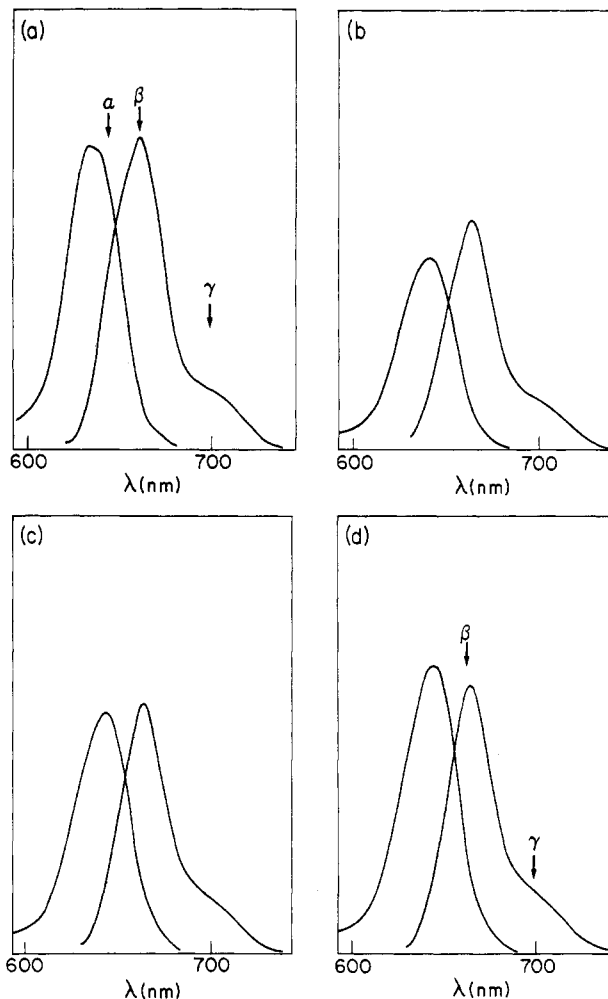


Figure 5. Corrected fluorescence excitation and emission spectra of (a) **2**, (b) **3**, (c) **4**, and (d) **5** in CH_2Cl_2 (concentration $\sim 3 \times 10^{-7} \text{ M}$).

study of squaraines.¹⁰ In that study, we also studied the chemical ionization mass spectrum of **1**, using CH_2Cl_2 as ionization gas. Ion peak at m/z 355, which corresponds to the $(\text{1:Cl})^-$ complex, was observed in the negative mass spectrum.

In addition to absorption spectroscopy and fluorescence spectroscopy, we have also studied the solute-solvent interactions of **4** in a variety of deuterated solvents by proton NMR spectroscopy.²⁸ The solvent effect on the chemical shifts of the aromatic protons of **4** was found to correlate with solvent parameter π^* and λ_{\max} of **4** as well as the fluorescence quantum yield. The ability of proton NMR data to correlate with the emission data further confirms that the multiple fluorescence emission of squaraine is derived from ground-state solute-solvent complexation.

3. Effects of Structural Changes on the Multiple Emission of Squaraines. N-Alkyl Group. Figure 5 shows the fluorescence emission and excitation spectra of **2**–**5** in methylene chloride. In each case, the excitation spectrum was found to be independent of the monitoring wavelengths and was identical with the absorption spectrum. The spectral results, which are summarized in Table II, show that *N*-alkyl groups exert a relatively minor bathochromic effect on the emission maxima (λ_F) of individual bands as compared to the λ_{\max} . The small shift is consistent with the MNDO calculation results by Bigelow and Freund, who showed that the CT on optical excitation is confined in the central C_4O_2 unit.⁹ As the chain length increases, the intensity of the α -band decreases. Only β - and γ -bands are observed in the fluorescence spectra of **4** and **5**. The gradual dominance of the β -emission suggests that the complexation constant between squaraine and solvent molecules increases as the length of the

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N-alkyl group increases. Since MO calculation showed that the central C_4O_2 unit becomes more polarized when the polarized charges in the anilino moiety are stabilized, the increase in complexation from $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5$ can be attributed to the increased polarization of the central C_4O_2 unit as the positive charges at the nitrogen atoms are stabilized by the electron-releasing *N*-alkyl groups. This interpretation is complemented by the results obtained from a solvent-effect study of the emission of **4**, where the complexation constant is also found to increase when the C_4O_2 unit is polarized by polar solvents (Figure 2).

The fluorescence quantum yields (ϕ_f) of **1–5** are high, in the range of 0.65–0.74. After correction from the γ -emission, the quantum yields of the $\alpha + \beta$ band ($\phi_{\alpha\beta}$) or the β -band (ϕ_β) of **1–5** are in the range of 0.58–0.66. As seen with later examples (**6–8**), the small increase in quantum yield as the size of the *N*-alkyl group increases can be attributed to the decrease in rate of rotational relaxation (around the C–C bond between the phenyl ring and the four-membered ring) of the excited state of squaraine, because the rate of this rotational relaxation process is expected to decrease as the size of the rotating group increases.

The γ -emission is usually resolvable from the α -emission and the β -emission. The ϕ_γ/ϕ_f values are found to be independent of the chain length ($\sim 12\%$). As seen in later discussion, both population and de-excitation of the relaxed excited state involve rotation of the C–C bond between the phenyl ring and the four-membered ring of squaraine; the constant ϕ_γ/ϕ_f values observed in **1–5** can be rationalized as a compensation effect between the population and the depopulation processes.

Effect of C-2 Methyl Group on the Fluorescence Emission of Squaraine and Discussion of the Origin of the γ -Emission. Major evidence for the spectral assignment of the γ -emission comes from the structural effect exhibited by the β -emission and the γ -emission of squaraines **6–8**. From the structural sensitivity of these two emission bands, we propose that the γ -emission is the emission from a relaxed, twisted excited state (to a twisted ground state). This model is supported by the structural effects observed in the multiple-emission bands of **15** and **16** and by the low-temperature spectrum of **4** at 77 K (Figure 3b).

The fluorescence emission spectra of **6–8** in methylene chloride are shown in Figure 6a–c. Again, the excitation spectra of these emissions are independent of monitoring wavelengths and are identical with their absorption spectra. Only β - and γ -bands are observed, and they are shifted by 400–600 and 1034–1376 cm^{-1} from their λ_{max} , respectively. As in **1–5**, a very small bathochromic effect is observed on the λ_F as the length of the *N*-alkyl chain increases.

The ϕ_f values of **6**, **7**, and **8** are 0.023, 0.036, and 0.054, respectively. After subtracting the γ -emission, the ϕ_β values of **6**, **7**, and **8** are 0.017, 0.024, and 0.032, respectively. These values are 20–30 times smaller than those of **1–4** and show a strong dependence on the *N*-alkyl group. The ϕ_γ/ϕ_f values of **6**, **7**, and **8** are 27, 34, and 40%, which are 2–3 times higher than those of **1–4** and also exhibit strong dependence on the *N*-alkyl group.

As discussed earlier under the absorption spectral data section, due to steric repulsion between the C-2 methyl group and the C–O group, **6–8** are nonplanar in methylene chloride solution. The absence of the α -emission in the emission spectra of **6–8** suggests that the loss in delocalization energy during the conformational change is probably compensated by the formation of the solute-solvent complex. In any event, excitation of **6–8** will result in a nonplanar excited state, which can either emit a photon to give the β -emission or can undergo radiationless decay via molecular relaxation processes.²⁹ Since Rettig and Gleiter³⁰ showed earlier that the rate for the formation of twisted intramolecular CT state increases considerably as the twisted angle of the ground state increases, the drastic decrease in the ϕ_β values of **6–8** and the strong dependences of the ϕ_β and the ϕ_γ/ϕ_f values on the alkyl

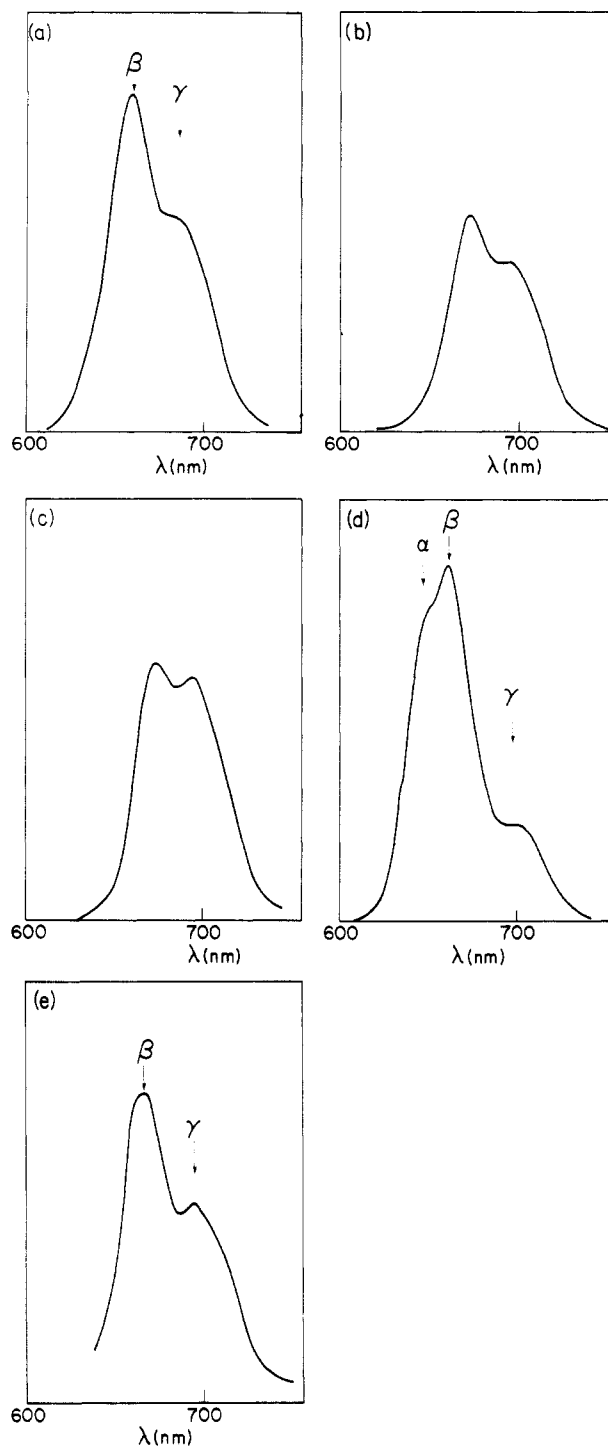


Figure 6. Corrected fluorescence emission spectra of (a) **6**, (b) **7**, (c) **8**, (d) **15**, and (e) **16** in CH_2Cl_2 (concentration $\sim 3 \times 10^{-7}$ M).

groups lead us to propose that the molecular relaxation process of the excited state of squaraine involves a C–C bond rotation between the phenyl ring and the four-membered ring (Scheme 1). Because of the nonplanarity of the excited states of **6–8**, C–C bond rotation in **6–8** is expected to be much faster than in the cases of **1–4**, resulting in the drastic decrease in ϕ_f values of **6–8**. The fact that the β -emission increases from $6 \rightarrow 7 \rightarrow 8$ is consistent with the rotational de-excitation mechanism because the rate of rotation is expected to decrease as the size of the rotating group increases. Very similar rotational de-excitation is also reported in the excited states of stilbenes,³¹ rhodamines,³² cou-

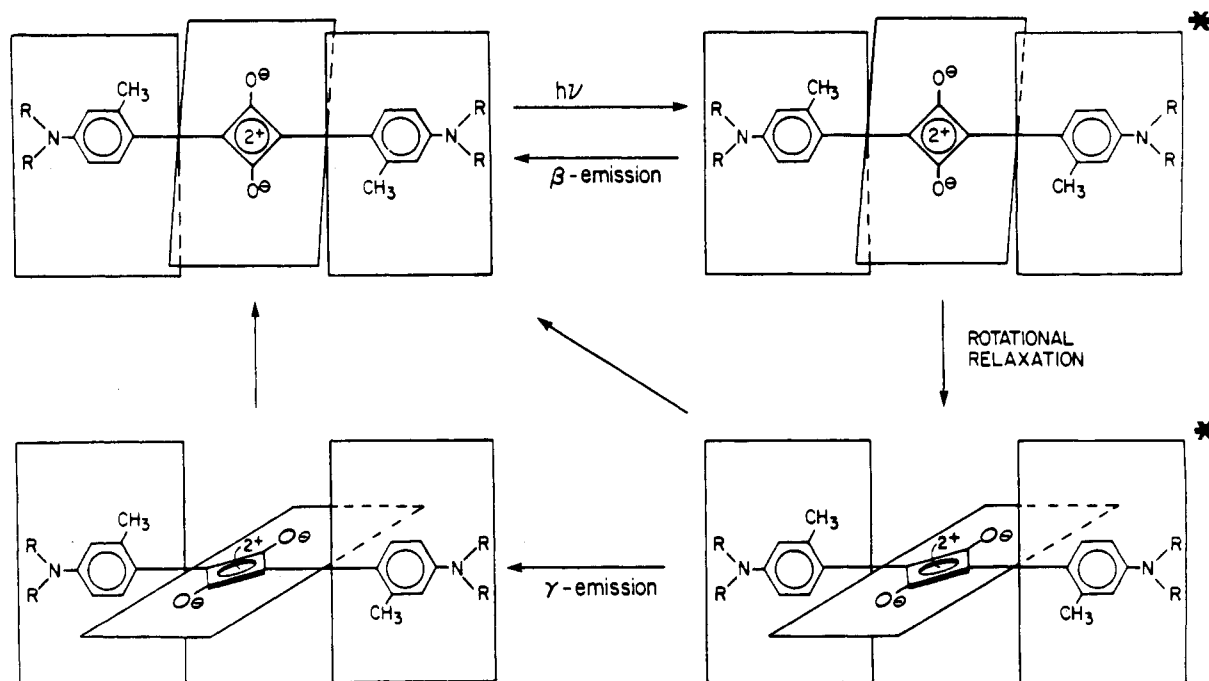
(29) Solvent effect studies show that ϕ_f (at room temperature) of **4** approaches unity in solvents where the rotational relaxation process is restricted. This result suggests that ϕ_{isc} is insignificant and rotational relaxation is the major radiationless decay process of the excited state of squaraine.

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SCHEME I



marins,³³ and *p*-(dimethylamino)benzonitriles and derivatives.³⁴ The fact that the molecular relaxation process does not involve any C–N bond rotation is complementary with the emission data of **18** and **19** which show that the photophysical processes of the excited states of **18** and **19** are very similar to those of **1** and **6** despite the C–N bond rigidization.

In Scheme I, we also propose that rotational relaxation of the excited state of squaraine results in the population of a relaxed, twisted excited state. This relaxed excited state either can emit a photon to give the γ -emission or undergoes a rotational relaxation to the ground state by rotation of the C–C bond between the four-membered ring and the phenyl ring. This proposition is consistent with the structural effect exhibited in the γ -emission of **6**–**8**. For example, there is a steady increase in contribution of the γ -emission, from 27 \rightarrow 34 \rightarrow 40% as the size of the *N*-alkyl group increases, even though the efficiency of populating the γ -state is about constant (95–98%).²⁹ The increase in γ -band contribution is explainable by the free rotor de-excitation mechanism analogous to that of the β -emission. In addition, the structural effect exhibited by the emission spectra of **15** and **16** also support the above model. For instance, the ϕ_β values of **15** and **16** decrease as the size of the C-2 substituent increases due to conformational effects, and the decrease of ϕ_β is accompanied with an increase in γ -band contribution in the emission spectrum.

Further support of the model in Scheme I comes from the low-temperature emission spectrum of **4** (Figure 3b). The absence of the γ -emission is then attributed to the prohibition of the C–C rotation at 77 K in ether matrix.

Fluorescence emission from a twisted relaxed CT state, commonly known as TICT emission, is actually a general photophysical phenomena for D–A molecules.^{25,35} One notable example is the dual fluorescence of DMABN.³⁶ The structural effect on the TICT emission of DMABN has been studied extensively by Grabowski and co-workers.³⁷ They showed that the intensity of the TICT emission increases when the D–A moiety is twisted from

planarity or visa versa. Nakashima et al.³⁸ and Rettig³⁹ studied the temperature effect on the dual fluorescence of DMABN; they found that the intensity of the TICT emission decreases as the temperature decreases, which is attributable to temperature effect on the twisting motion. The similar structural and temperature effects exhibited by the dual fluorescence of DMABN and by the β - and the γ -emissions of squaraine not only confirm that the γ -emission in this work is an analogue of the TICT emission but also show that, despite having a D–A–D structure, the photophysical behavior of squaraine is no different from other D–A molecules.

It is, however, worth noting that, in contrast to the TICT emission of DMABN, the wavelength of the γ -emission of squaraine is insensitive to structural changes and solvent polarity (Figures 1, 3, and 5–8). The insensitivity of the γ -emission toward *N*-alkyl and C-2 substituents is not particularly surprising in view of the lack of structure effects on the wavelengths of the α - and the β -emissions (Table II). Since MNDO calculations⁹ show that the CT between the S_0 and the S_1 states of squaraine is confined primarily in the central C_4O_2 unit, the structural insensitivity of the γ -emission can thus be attributed to the minor involvement of the D moiety in the electronic transition. The lack of solvent effect on the γ -emission is somewhat unexpected because of the high polarizability of the charges in the squaraine structure. An extensive solvent-effect study on the emission spectra of **4**²⁸ shows that the solvent insensitivity is a genuine property of the α -, the β -, and the γ -emissions of squaraine. We believe that our unique observation is probably, in part, due to the symmetric D–A–D structure of squaraine, which results in zero dipole moment in the ground and the excited CT states. Moreover, as a result of the similar charge distributions in the S_0 and the S_1 states,⁹ reorganization of solvent molecules during an electronic transition is small. The small Stokes shifts observed in the emission spectra of **1**–**19** is already indicative of a small solvent reorganization. The lack of solvatochromic shift on the multiple-emission bands is therefore not an inconsistent observation. Details of the effect of solvent on the fluorescence emission of squaraine will be reported in a forthcoming report.²⁸

Effect of C-2 F, C₂H₅, OH, and OCH₃ Substituents. *a.* $X = F$. The fluorescence spectrum of **15** is presented in Figure 6d. Three emission bands, α , β , and γ , are observed, and they are

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shifted by 536, 756, and 1608 cm^{-1} , respectively, from the λ_{max} . The ϕ_f of **15** is 0.091, and the ϕ_γ/ϕ_f value is 17%. The decrease in ϕ_f and the increase in ϕ_γ/ϕ_f in **15** as compared to **1** is attributable to the free rotor effect as described in Scheme I. The smaller magnitude of the decrease in ϕ_f and on the increase in ϕ_γ/ϕ_f in **15** as compared to **6** correlates with the smaller size of the fluorine atom.

b. $X = \text{C}_2\text{H}_5$. The fluorescence spectrum of **16** is shown in Figure 6e. As in the spectra of **6–8**, only β - and γ -bands are observed, and they are shifted by 616 and 1368 cm^{-1} from the λ_{max} , respectively. The ϕ_f of **16** is 0.024; after correcting for the γ -emission, ϕ_β becomes 0.014. The slight decrease in the ϕ_β of **16** as compared to that of **6** is attributed to the faster rotational relaxation of the excited state of **16** (to the relaxed excited state) due to the greater nonplanarity induced by the ethyl group.

The ϕ_γ/ϕ_f of **16** is 40%. Because of the low quantum yield of intersystem crossing from S_1 to T_1 ,²⁹ the efficiency of populating the relaxed excited state between **16** and **6** should be very similar (98.6% for **16** and 97.7% for **6**). The increase in ϕ_γ/ϕ_f of **16** as compared to **6** is thus significant. Since rotational relaxation is also shown to be a major radiationless decay process for the relaxed excited state (Scheme I), the substantially higher ϕ_γ/ϕ_f in **16** as compared to that of **6** is attributed to the greater retardation of the C–C rotation in the relaxed excited state of **16** due to the steric repulsion between the ethyl group and the C–O group when a planar conformation is approached.

c. $X = \text{OH}$. The fluorescence spectra of **12–14** are given in Figure 7a–c. Three emission bands (α , β , and γ) are observed in the emission spectrum of **12**, and only two bands (β and γ) are observed in the spectra of **13** and **14**. The gradual dominance of the β -emission, along with the bathochromic shift on λ_{max} , as the length of the *N*-alkyl group increases, suggests that, as a result of the increased polarization in the D–A–D structure, more solute–solvent complexes are formed. This observation is identical with that seen in **1–5**.

The ϕ_f values of **12–14** are ~ 0.83 – 0.86 , and the ϕ_γ/ϕ_f values are $\sim 12\%$. The constant ϕ_f and ϕ_γ/ϕ_f values among **12–14** are in contrast to those observed in **1–8**. Molecular model study shows that intramolecular H-bonding between the C-2 OH group and the C–O group in the four-membered ring should be feasible throughout a full rotation of the C–C bond between the phenyl ring and the four-membered ring. Thus, the high ϕ_f values and their independence on the *N*-alkyl group can be attributed to the H-bonding effect. Due to the dominant influence of the rotational relaxation processes by H-bonding, the photophysics and the emission spectra among **12–14** are very similar.

d. $X = \text{OCH}_3$. The fluorescence spectra of **9–11** are given in Figure 7d–f. Three emission bands (α , β , and γ) are observed in the emission spectrum of **9**, and two emission bands (β and γ) are observed in the spectra of **10** and **11**. The *N*-alkyl effect in **9–11** is identical with those observed in **1–5** and **12–14**.

The ϕ_f values of **9**, **10**, and **11** are 0.042, 0.049, and 0.26, respectively. After correction for the γ -emission, $\phi_{\gamma\beta}$ of **9** and ϕ_β of **10** and **11** become 0.034, 0.035, and 0.22, respectively. These $\phi_{\gamma\beta}$ or ϕ_β values are higher than those of **6–8** but lower than those of **1–4**. Since rotational relaxation is the dominant radiationless decay process of the excited state of squaraine, our quantum yield results thus suggest that methoxysquaraines **9–11** are closer to planarity in the ground state than those of **6–8** despite the bulkier methoxy groups. The increased planarity in **9–11** as compared to **6–8** may be the result of the CT stabilization of the D moiety by the electron-releasing methoxy group, which probably flattens the squaraine structure despite steric hindrance.

The ϕ_γ/ϕ_f values of **9**, **10**, and **11** are 18, 29, and 17%, respectively, and are in contrast to the results of **6–8**, where ϕ_γ/ϕ_f increases as the chain length increases. Although the increase in ϕ_γ/ϕ_f from **9** to **10** can be explained by the free rotor mechanism in Scheme I, the small ϕ_γ/ϕ_f value in **11** is unexpected. Since the planarity of a squaraine should increase as the D–A–D CT character increases, the drastic increase in ϕ_f of **11** relative to **9** and **10** as well as **8** suggests that **11** is the most planar molecule among them. Hence, rotational relaxation of the excited state

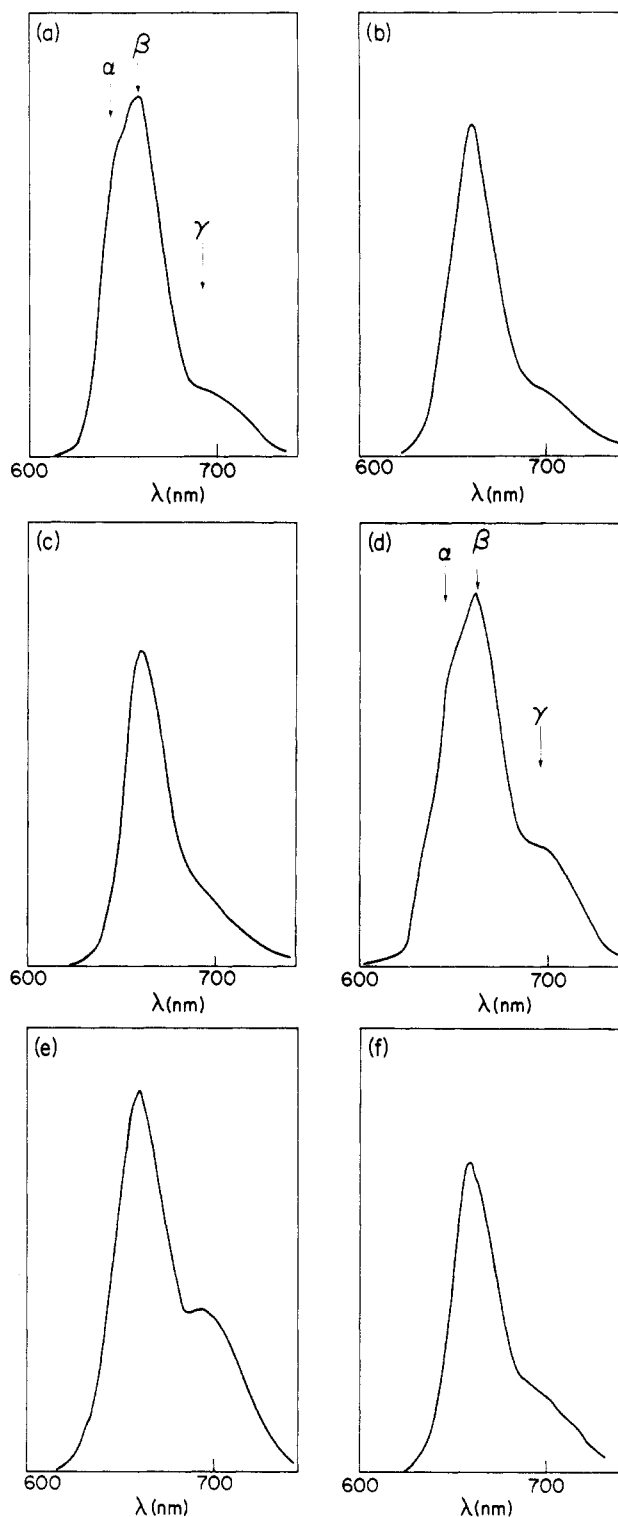


Figure 7. Corrected fluorescence emission spectra of (a) **12**, (b) **13**, (c) **14**, (d) **9**, (e) **10**, and (f) **11** in CH_2Cl_2 (concentration $\sim 3 \times 10^{-7}$ M).

of **11** becomes the slowest, resulting in higher ϕ_f and lower ϕ_γ/ϕ_f values. The deviation in photophysical behavior of **11** relative to **9** and **10** is thus a conformational effect.

Effect of C-3 Substituents. The fluorescence spectra of **17–19** are shown in Figure 8a–c. Squaraine **17** exhibits three emission bands which are shifted by 229, 518 and 1700 cm^{-1} from its λ_{max} , and they are assigned to the α -band, the β -band, and the γ -band, respectively. The ϕ_f of **17** is 0.49 and is $\sim 30\%$ lower than that of **1**. Since absorption spectral data suggest that the *N,N*-dimethylamino group of **17** is twisted out of the molecular plane of squaraine by steric repulsion, the low ϕ_f value is probably the result of the free rotor de-excitation of the excited state of **17** by rotation of the already twisted C–N bonds.

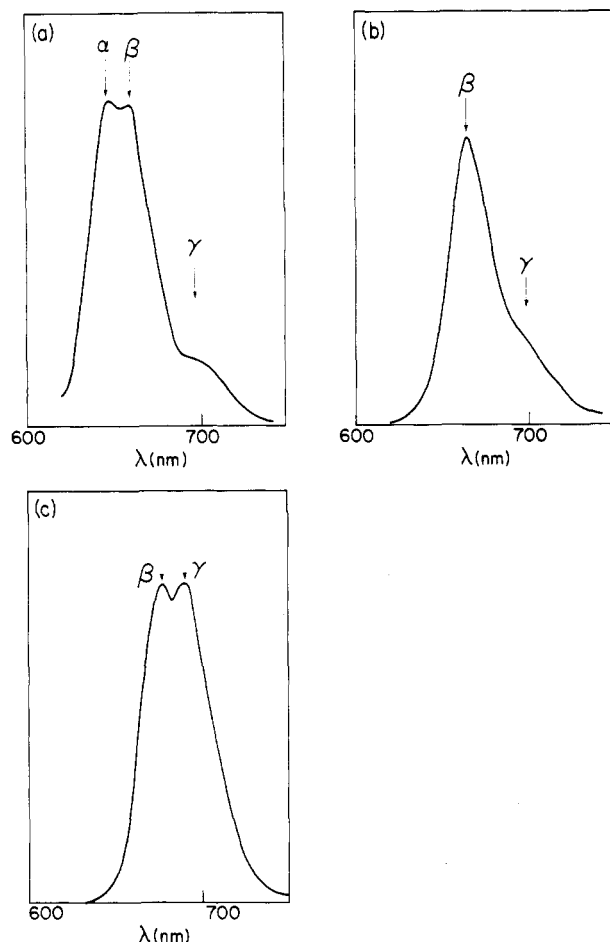


Figure 8. Corrected fluorescence emission spectra of (a) **17**, (b) **18**, and (c) **19** in CH_2Cl_2 (concentration $\sim 3 \times 10^{-7}$ M).

Only two emission bands are observed in the fluorescence spectra of **18** and **19**, and they are assigned to the β -band and the γ -band in accordance with their Stokes shifts.⁴⁰ The ϕ_f values of **18** and **19** are 0.42 and 0.32, respectively. After correction for the γ -emission, the ϕ_β values of **18** and **19** become 0.38 and 0.16, respectively. Our results suggest that there is a steady decrease in ϕ_β , despite the increased C–N bond rigidity from **1** \rightarrow **18** \rightarrow **19**. This observation actually complements the fact that rotation of the C–C bond is the major molecular relaxation process of the excited state of squaraine. Since emission data show that **18** and **19** exist as solute–solvent complexes in methylene chloride solution (Figure 8b,c), and since it is known that nonplanarity

is generally induced in this complexation process, the decrease in ϕ_β from **1** \rightarrow **18** \rightarrow **19** is thus a conformational effect, where the rate of C–C bond rotation increases as the twisted angle of the ground state increases.³⁰ More detailed investigation on the electronic spectra of **19** is in progress.

The ϕ_γ/ϕ_f values of **17** and **18** are about 11% and are similar to those of **1**–**5**. On the other hand, the ϕ_γ/ϕ_f values of **19** are anomalously high, $\sim 50\%$. The increase in ϕ_γ/ϕ_f can also be explained by a conformational effect. For instance, because **19** is not planar in the ground state in solution due to the solute–solvent complex formation, there is an increase in population of the twisted, relaxed excited state after electronic excitation. Since rotational relaxation of this twisted relaxed excited state to planarity is retarded by geometrical factors, an increase in γ -emission results. The observed high ϕ_γ/ϕ_f value for **19** appears to be reasonable.

Concluding Remarks

The spectroscopic properties of a class of donor–acceptor–donor charge-transfer molecules, squaraines, have been studied. Squaraines exhibit sharp and intense absorption ($\epsilon \sim 3 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$) in the red in methylene chloride solution. Small bathochromic shifts are observed for all the substituents studied in this work. The small shift, which is due to the minor involvement of the D moiety in the electronic transition, is shown to primarily originate from the solute–solvent complex.

Multiple emission is observed in the fluorescence spectra of squaraines. The intensities of individual bands are found to be sensitive to the structure of the molecules, the solvent, and the ambient temperature. Three emission bands, namely, α , β , and γ , are identified and are shifted by 200–400, 530–780 and 1400–1700 cm^{-1} from the absorption λ_{max} . From preliminary solvent-effect and temperature-effect studies, we have been able to show that squaraines form solute–solvent complexes in organic solvents. The equilibrium constant of complex formation increases as the D–A–D CT character increases. Thus, excitation of squaraine in solution results in two kinds of excited states: the excited state of free squaraine and the excited state of the solute–solvent complex. These two excited states, which are in rapid equilibrium, emit photons to give the α -emission and the β -emission, respectively. Rotational relaxation(s) is (are) found to be the major radiationless decay process(es) of these two excited states. As a result of the C–C bond rotation, a twisted relaxed excited state is generated. This twisted excited state can emit a photon to give the γ -emission, or it can relax by rotation of the C–C bond to the ground state. Dynamic experiments which are expected to give a quantitative picture on the photophysical processes of squaraines will be pursued.

Registry No. **1**, 43134-09-4; **2**, 82930-30-1; **3**, 105810-36-4; **4**, 99663-97-5; **5**, 109976-92-3; **6**, 63842-82-0; **7**, 102128-66-5; **8**, 105810-37-5; **9**, 105810-38-6; **10**, 105810-39-7; **11**, 109976-93-4; **12**, 63842-83-1; **13**, 68842-66-0; **14**, 87286-91-7; **15**, 98125-61-2; **16**, 105856-84-6; **17**, 109976-95-6; **18**, 72907-70-1; **19**, 68842-56-8.

(40) The α -bands of these compounds are discernible in diethyl ether, a weak complexing solvent.